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BIOLOGICAL TREATMENT TECHNOLOGY (162)

ENVIRONMENTAL PROTECTION AGENCY

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This manual includes a collection of instructional materials to assist the student to upgrade performance of biological treatment facilities. Information gathering techniques related to wastewater characteristics, concentrations, and loading are described. The influence of these data upon common treatment operations and correction of treatability difficulties are considered. Operational control to maximize the performance of existing facilities are discussed along with selection of add-on operations or design of new facilities to upgrade the treatment system to a performance compliance status.

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BIOLOGICAL TREATMENT TECHNOLOGY

This course is designed for engineers, chemists, biologists, bacteriologists, and other administrative personnel responsible for the planning and conduct of water pollution surveys.

ENVIRONMENTAL PROTECTION AGENCY
Water Program Operations
TRAINING PROGRAM

FOREWORD

These manuals are prepared for reference use of students enrolled in scheduled training courses of the Water Program Operations, Environmental Protection Agency.

> *Due to the limited availability of the manuals, it is not appropriate to cite them as technical references in bibliographies or other forms of publication.*
>
> *References to products and manufacturers are for illustration only; such references do not imply product endorsement by the Office of Water Programs, Environmental Protection Agency.*

The reference outlines in this manual have been selected and developed with a goal of providing the student with a fund of the best available current information pertinent to the subject matter of the course. Individual instructors may provide additional material to cover special aspects of their own presentations.

This manual will be useful to anyone who has need for information on the subjects covered. However, it should be understood that the manual will have its greatest value as an adjunct to classroom presentations. The inherent advantages of classroom presentation is in the give-and-take discussions and exchange of information between and among students and the instructional staff.

Constructive suggestions for improvement in the coverage, content, and format of the manual are solicited and will be given full consideration.

TRAINING PROGRAM

Through the Office of Water Program, Environmental Protection Agency conducts programs of research, technical assistance, enforcement, and technical training for water pollution control.

Training is available at five installations of the Agency. These are: the National Training Center located at the Robert A. Taft Sanitary Engineering Center in Cincinnati, Ohio; the Robert S. Kerr Water Research Center, Ada, Oklahoma; the Southeast Water Laboratory, Athens, Georgia; the Pacific Northwest Water Laboratory, Corvallis, Oregon; and the Hudson-Delaware Basins Office, Edison, New Jersey.

The objectives of the Training Program are to provide specialized training in the field of water pollution control which will lead to rapid application of new research findings through updating of skills of technical and professional personnel, and to train new employees recruited from other professional or technical areas in the special skills required. Increasing attention is being given to development of special courses providing an overview of the nature, causes, prevention, and control of water pollution.

Scientists, engineers, and recognized authorities from other Agency programs, from other government agencies, universities, and industry supplement the training staff by serving as guest lecturers. Most training is conducted in the form of short-term courses of one or two weeks' duration. Subject matter includes selected practical features of plant operation and design, and water quality evaluation in field and laboratory. Specialized aspects and recent developments of sanitary engineering, chemistry, aquatic biology, microbiology, and field and laboratory techniques not generally available elsewhere, are included.

The primary role and the responsibility of the States in the training of wastewater treatment plant operators are recognized. Technical support of operator-training programs of the States is available through technical consultations in the planning and development of operator-training courses. Guest appearances of instructors from the Environmental Protection Agency, and the loan of instructional materials such as lesson plans and visual training aids, may be available through special arrangement. These training aids, including reference training manuals, may be reproduced freely by the states for their own training programs. Special categories of training for personnel engaged in treatment plant operations may be developed and made available to the States for their own further production and presentation.

An annual Bulletin of Courses is prepared and distributed by the Office of Water Programs. The Bulletin includes descriptions of courses, schedules, application blanks, and other appropriate information. Organizations and interested individuals not on the mailing list should request a copy from one of the training centers mentioned above.

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BIOLOGICAL TREATMENT TECHNOLOGY

I This course is designed for graduate engineers and scientists now engaged in or about to be involved in planning, design of facilities, upgrading operation of existing facilities, and other responsibilities associated with biological renovation of wastewater.

II Course objectives include comprehensive consideration of the strong points and limitations of aerobic and anaerobic biological water renovation processes, the variations most likely to affect performance, and the means to control process performance. The student is intended to acquire an improved capacity to match the situation and the process selection, to enhance the quality of reusable water to meet Water Quality Standards.

III Course work will be distributed along the following major headings.

A Characteristics of microbial activity will be related to the theory of design for aerobic and anaerobic biological stabilization processes.

B Means of procurement for information needed to select processes, design facilities and to improve performance efficiency will include consideration of past history, projected activities of the contributing population, nature of the load, available processes, possible process and operational improvements, and current stress in process development.

C The means of filling information gaps will be stressed. The advantages and limitations of laboratory, bench scale, pilot scale and full scale experimentation will be considered along with the guidelines of experimental design and extrapolation of information from one situation to another to improve cost/benefit ratios.

D Performance evaluation methods will be considered as a means to more realistically determine what is being done and to upgrade performance in line with what may be done. Better performance evaluation also will be useful to suggest alternate procedures, advantageous before, during, after, or in place of conventional biological processes.

IV Students will evaluate data on a variety of treatability concepts and methods of obtaining pertinent information showing relationships among:

A Effects of used water contaminant type, amount, concentration, load variation, temperature, time, etc., upon biological processes.

B Methods of experimental design and equipment used for treatability evaluation for various wastes will be presented. Several experimental approaches will be considered in terms of the effects of biodegradation on the test waste, the effects of the test waste upon treatment processes, or upon associated wastewater components. Guidelines for determining differences among small and large scale units will be used to indicate the nature of information susceptible to transfer from small to full scale units and that which cannot be so readily transferred.

C Various treatment processes including ponds, trickling filters, activated sludge, anaerobic, facultative or aerobic processes and various modifications thereof will be discussed to clarify desing, control and operational feasibility in representative situations.

D Tests and measurements pertinent to water renovation will be discussed in terms of applicability for information retrieval and performance evaluation.

E Workshop problem sessions will be used for familiarization with data presentation and recovery for design and application purposes. The problem sessions are intended to focus attention upon what is or is not available among information resources required to meet objectives. Group discussion will be used to develop guidelines useful for applications and to clarify relationships between theory and practice. Many concepts are believed to be understood; the test lies in application.

F Both theoretical and empirical approaches will be used in an attempt to blend requirements and situations within a realistic cost/benefit ratio.

G A major fraction of course topics deals with municipal wastewater treatment and nonpollutional disposal. Certain industrial wastewater situations will be considered in terms of their effects upon conventional treatment and the design process, or control modifications required to adapt treatment to nonideal real situations.

H Course presentations will stress versatility in design, operation and performance necessary to meet changing quality requirements and increased and changing loading. Means will be stressed whereby performance may be upgraded by improved use of existing capacity, supplemented by alternate unit operations in series, parallel or other means of doing the job with a more favorable ratio of concrete and equipment for operational costs.

V The course will be conducted in an informal manner including lecture, demonstration, discussion and workshop sessions of selected topics.

A Speakers and staff will encourage maximum group participation and speaker-student relationship of an on-topic nature.

1 Questions or comments are solicited which will increase understanding of the subject and clarify topic concepts among the group.

2 Discussion time will be available for each topic speaker. Additional time will be available during workshop sessions or by special arrangement with available sources of information.

3 Discussion time will be as liberal as possible within the constraints of scheduling following speakers and general interest.

B Manual outlines are prepared for your use as background information and recall purposes. The speaker is encouraged to present current stress and case situations, hence may or may not follow the outline format precisely. Students are urged to review the topic outline for content prior to the presentation insofar as possible.

C Staff and invited speakers are there to help you. If you don't obtain the answer sought, it will not be because they didn't try. The information sought may be unavailable or dependent upon conditional variables requiring more consideration than practical for a group approach. Hopefully, they will be able to cite sources of additional information for you. If you do not succeed the first time, try again.

This outline was prepared by F. J. Ludzack, Chemist, National Training Center, WPO, EPA, Cincinnati, OH 45268.

NUTRIENTS: THE BASIS OF PRODUCTIVITY

I INTRODUCTION

A Nutrients of importance include macronutrients: those needed in large quantities, and micronutrients: those needed in small amounts.

B These nutrients are important because they promote biological responses which may interfere with some desired use of the water by man.

C Other factors (e.g. temperature, light) affect the use of these nutrients and should be considered in an evaluation of the effects of nutrients upon the ecosystem.

II Algae, bacteria, fungi and aquatic plants are the forms of life which nutrients affect most directly.

A Algae are of Several Types

1 Phytoplankton are small algae suspended in the water and form the basis of productivity in the aquatic environment.

2 Benthic algae are those forms anchored to substrates of rock and bottom materials.

3 Periphytic algal are those microscopic forms attached to submersed substrates.

B Aquatic plants are of several types. In general they may be referred to as rooted or floating forms.

C Heterotrophic bacteria are fungi which respond to organic nutrients introduced into water. Autotrophic bacteria may respond and grow due to inorganic nutrient sources.

III BIOLOGICAL LAWS

A Liebig's "law" of the minimum: the essential material available in amounts most closely approaching the critical minimum needed will tend to be the limiting factor.

B Shelford's "law" of tolerance: survival of an organism can be controlled by the quantitative or qualitative deficiency or excess with respect to any one of several factors which may approach the limits of tolerance for that organism.

C Q_{10} "law": with a temperature increase of 10 degrees centigrade metabolic processes (rates) are approximately doubled.

IV The process of photosynthesis is the fixation of the sun's energy with the production of organic matter by plants with chlorophyll.

A The general reaction is given below:

$$CO_2 + H_2O \xrightarrow{\lambda} CH_2O + O_2$$

B Chlorophyll contains basically C, O, H, N and Mg, and in general makes up about 5% of the dry weight of algal cells.

V MEASUREMENT OF PHOTOSYNTHESIS

A Oxygen production can be used as a measure of photosynthesis because for each mole of CO_2 reduced to organic carbon one mole of free oxygen is liberated.

1 The value of the molar O_2/CO_2 ratio has been found experimentally to vary within wide limits.

B CO_2 Assimilation

1 The CO_2 taken up by algae does not all originate from the dissolved gas. Some algae can use bicarbonate directly as a source of carbon.

2 Hence measurement of CO_2 uptake from water is a complicated problem which must consider pH, HCO_3^-, and $CO_3^=$ concentrations.

C Fixation of Carbon-14

1 The use of C^{14} as a tracer of C^{12} in plant metabolism and productivity estimation has been widely used since the early nineteen fifties.

2 In this method a known amount of C^{14} is added to the water and after a period of time the proportion of C^{14} in the plant cells to C^{14} added is found. The amount of carbon assimilated is then estimated from the following equation.

$$\frac{\text{activity of phytoplankton}}{\text{activity of } C^{14}O_3^= \text{ added}} \text{ (K)} = \frac{\text{total carbon assimilated}}{\text{total carbon available}}$$

3 Where K is a constant relating to the slower uptake of C^{14}.

4 The total carbon available is determined chemically.

D Uptake of Mineral Nutrients

1 The measurement of depletion of nutrients in solution has been tried but found unreliable.

E Chlorophyll

1 The quality of chlorophyll present has been found to bear some relation to productivity but not a reliable one.

VI Nutrients of significance in the growth and production of algae and plants are discussed below.

A Carbon

1 Sources

a Gaseous CO_2

b HCO_3^-

c $CO_3^=$

d Other carbon compounds

2 Effects of the removal of carbon upon the water

a Lowered pH

b Deposition of $CaCO_3$

3 The quantity of carbon available is great and it usually is not a limiting factor.

B Nitrogen

1 Nitrogen can be taken up by most algae as either ammonium salts or as nitrates. Nitrites can also be used but a high concentration is usually inhibitory. Some blue green algae can fix atmospheric nitrogen. Certain algae varieties require supplementary amines, growth factors, etc.

2 The quantity of nitrogen in waters has definitely been shown to limit algal populations.

C Phosphorus

1 Phosphate seems to be the only inorganic source of this nutrient.

2 Limiting concentrations of P have been found to range from .01 ppm at a minimum and an inhibitory affect if P concentrations exceed 20 ppm.

3 Optimum concentrations have been found to range from .018 ppm to 15 ppm.

4 Storage of inorganic phosphate by algae has been demonstrated. The extent of this storage may reach 80% of the total phosphorus in algal cells.

D Silicon

1 Nutrient ratios in the algal cells of some areas have been found to be Si 23: N16: P1. It can be seen from this ratio that silicon is an important element in algal growth.

2 Silicon is especially important in the population growth of diatoms and may be the limiting growth factor in these populations.

E Inorganic micronutrients - Many elements are needed in very small quantities by algal cells. Some of these have a known function in algal metabolism; others do not.

1 Mg is a cation of major importance in the chlorophyll molecule.

2 Co is known to be necessary for vitamin B_{12}.

3 Mn is necessary for several enzyme systems.

4 Mo, V, Zn, and Cu are necessary but these functions are not as well known.

F Organic Micronutrients

1 Of 179 algal strains investigated about 40% required vitamin supplementation for optimum growth. Principal growth factors that were not synthesized in sufficient quantity are given as follows along with the percentage of the vitamin deficient strains showing marked productivity gain after supplementation:

a B_{12} addition increased growth on 80% of the strains.

b Thiamin addition increased growth on 53% of the strains.

c Biotin addition increased growth on 10% of the strains.

2 Algae can use and may require many organic compounds depending upon environmental conditions and the ability of the organism to synthesize required building blocks from mineral forms of C.N. & P. This is an area for continued investigation with many unappreciated or vaguely understood ecological factors.

VII PROBLEMS AND BENEFITS RESULTING FROM ALGAE PRODUCTION

A Problems to man may result when the total "primary production" by algae leads to an increase in the total organic content of the water that interferes with a desired use.

1 This may consist of a high algal population that produces a water with high turbidity, taste and odor, or other undesirable effect. High respiratory needs may lead to nocturnal oxygen deficit.

2 Certain algae may cause tastes and odors, clog filters; or otherwise interfere with potable water processing.

3 Death of large algal populations may lead to tastes and/or odors through bacterial decomposition. Oxygen deficits may result at any time of day in this process. Deposition of masses of organic sediment or sludge may be considerable.

4 Other problems might be cited.

B The primary production of algae can also serve as a supply of food to consumer organisms (animals), resulting in increased production at several (trophic) levels:

zoömicrobes, microinvertebrates, macroinvertebrates, fishes.

1 Earlier notation cited the release of oxygen during utilization of CO_2 during algal photosynthesis. This encourages fungal or bacterial breakdown of pollutants.

2 Photosynthesis occurs in the presence of adequate light and favorable conditions. In darkness, the cells continue to respire and may consume more oxygen than they produced because photosynthesis increases the organic load.

3 Photosynthesis tends to occur at the surface where light intensity is greatest. Poor vertical mixing would result in stratification of water supersaturated with oxygen over oxygen deficient water. Depending upon conditions, a significant fraction of the oxygen could be lost to the atmosphere.

4 Increased productivity may result in temporary reduction of the free dissolved nutrient level in the water but harvesting at some level is essential to prevent later recycle.

VIII CYCLE OF NUTRIENTS

A Once nutrients enter a body of water they are cycled through a food chain.

B Factors affecting this food chain (e.g. toxicity, removal) will affect the concentration and distribution of the nutrients.

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This outline was prepared by Michael E. Bender, Biologist, Formerly with Training Activities, Ohio Basin Region, SEC.

BIOASSAY AND BIOMONITORING

I INTRODUCTION

A An assay is an evaluation.

B A bioassay is an evaluation in which living organisms provide the scale.

1 The scale or degree of response may be the rate of growth or decrease of a population, colony, or individual; a behaviorial, physiological, or reproductive response, or simply a live or no-live response.

2 All types of bioassays may have a role to play in water quality evaluation at one time or another.

3 The particular group of bioassays discussed below are those which contribute to the evaluation of the effects of liquid wastes on aquatic environments in which experimental organisms such as fish are subjected to a series of concentrations of a known or suspected toxicant under adequately controlled conditions for a stipulated period of time.

C Historical Highlights

1 Prior to 1940, there was little or no uniformity in performing or reporting bioassays of water pollutants.

2 By mid-forties, the need for a standardized technique was becoming painfully obvious.

a The Atlantic Refining Company privately published the first statement of what is today, basically, our standard method (Hart, Doudoroff, and Greenbank, 1945).

b This was refined and accorded wide (but not universal) industrial, academic, and governmental acceptance in 1951 (Doudoroff, et al, 1951).

3 This method was first developed for the use of fishes, but has been found adaptable to a wide variety of organisms.

D Other Types or Plans of Bioassay

1 Many other designs for the expression of toxicity have been devised such as those based on time-concentration curves. Each has its advantages and proponents, but the basic Standard Method design remains the most widely used.

a In situ exposure of experimental organisms in cages or live cars, at selected sites above and below a suspected point or pollution is an obvious and time tested procedure, but lacks the precision of laboratory tests. It has the advantages of popular appeal, and of expressing actual environmental conditions.

b The familiar BOD test is a bioassay of the organic content of water subject to biodegradation.

E Biomonitoring

Water quality surveillance or monitoring by means of observing biota can be considered from two aspects: field and laboratory. It differs from bioassay primarily in the objective: a bioassay is an attempt to determine a specific defined value or threshold, whereas a biomonitoring operation is an attempt to use living organisms to ascertain whether or not aquatic life is endangered.

1 Periodic biological field surveys, samples, or other observation may demonstrate recent excessive pollution for example.

2 Organisms in a series of flow-through tanks in a laboratory may demonstrate the occurrence of an unacceptable

increase in the toxicity of an effluent, without measuring "how much" or "what."

II THE STANDARD METHOD BIOASSAY

A Introduction

1 This procedure is intended for use by industrial and other laboratories.

2 Its objective is to evaluate the toxicity of wastes and other water pollutants to fish or other aquatic organisms.

3 Potential applications are numerous.

  a Dilution and/or treatment necessary to avoid acute toxic effects can be estimated.

  b The efficacy of an existing treatment can be tested.

  c The potential usefulness of a proposed treatment can be estimated.

4 The design of the test need not involve a chemical knowledge of the toxicant.

  a Synergism, antagonism, and other interactions of chemical components cannot always be anticipated, but are automatically included in the result.

  b All chemical and physical information available is, however, essential to the adequate interpretation and application of test results.

5 The test is best used for local application. Generalizations should be made with great caution.

6 Field observations should be made of results of application over a significant period of time.

7 Careful distinction should be made between fish mortality due to a physiological toxicant, and that due to lack of DO.

8 A uniform testing procedure is essential to effective action in water pollution control.

B Routine Procedure for Static Tests

1 Test organisms should be fish or other organisms of local significance.

  a The most sensitive species available should be selected, but:

  b They should be species which are amenable to captivity.

  c They should be accurately identified.

  d They should be relatively uniform in size. Individuals less than 3 inches in length are usually most convenient.

  e They should be healthy and thoroughly acclimated to the laboratory.

  f A careful record should be kept of their origin, handling, and condition.

2 Test water should preferably be taken from the receiving stream just above the discharge being evaluated or in a lake or estuary, beyond the influence of the discharge.

  a If this is unsuitable, cleaner but similar waters from a more remote station may be substituted.

  b Artificial "standard" waters are not recommended for general use, although many formulae have been proposed.

  c In estuarine situations, a series of tests (marine grid) should be run, using waters of high and low salinities as characteristic of the region.

3 Other experimental conditions

a Temperature. The tests should be performed at a uniform temperature in the upper part of the expected summer range, e.g., 25 ± 2°C for warm water fish, and 15 ± 2°C for cold water species.

b Test containers should be of glass, widemouthed "pickle jugs" or battery jars are satisfactory. Five and one gallon sizes are both useful, but the larger size is required for conclusive results.

c Artificial aeration should not be used to maintain the dissolved oxygen concentration. If this falls below approximately 4 or 5 ppm at any time during the test, fewer fish should be used per container or an auxiliary oxygenation procedure invoked that is designed to avoid undue loss of volatile toxicants.

d The number of test animals should not be less than 10 per concentration for reliable conclusions; these may be distributed between two or more containers.

e Ratio of fish to solution. There should be not more than one gram of fish per liter of test solution.

4 Experimental procedure

a All dilutions for a given run should be prepared from the same sample.

b Duration. Tests should be run for at least 48 hours, preferable 96.

c Dead fish should be removed as soon as observed. Survivors should be counted and recorded each 24 hours.

d Feeding during the test should be avoided.

e Experimental concentrations. Any appropriate series of concentrations may be used. A logarithmic series such as is suggested in Table I is very convenient.

TABLE I

A Guide to the Selection of Experimental Concentrations, Based on Progressive Bisection of Intervals on a Logarithmic Scale.

Col. 1	Col. 2	Col. 3	Col. 4	Col. 5
10.0	----	----	----	----
----	----	----	----	8.7
----	----	----	7.5	----
----	----	----	----	6.5
----	----	5.6	----	----
----	----	----	----	4.9
----	----	----	4.2	----
----	----	----	----	3.7
----	3.2	----	----	----
----	----	----	----	2.8
----	----	----	2.4	----
----	----	----	----	2.1
----	----	1.8	----	----
----	----	----	----	1.55
----	----	----	1.35	----
----	----	----	----	1.15
1.0	----	----	----	----

Effluents of unknown, mixed, or variable composition are usually best expressed as percent by volume; while pure substances, or specific analyzable components are usually expressed as milligrams per liter (ppm). A control or reference tank containing dilution water only (with no toxicant) is essential, to demonstrate that all experimental organisms would have survived had it not been for the toxicant being tested.

f Expression of results. The measure of relative toxicity is the tolerance limit (symbol: TL). The time of exposure "t" must be shown along with the percentage of fish surviving (written as a postscript). For example, a 96 hour TL50 (optional: $TL50^{96\ hr}$) of a toxic substance is that concentration in which 50% of the experimental organisms survive for 96 hours. (Figure 1)

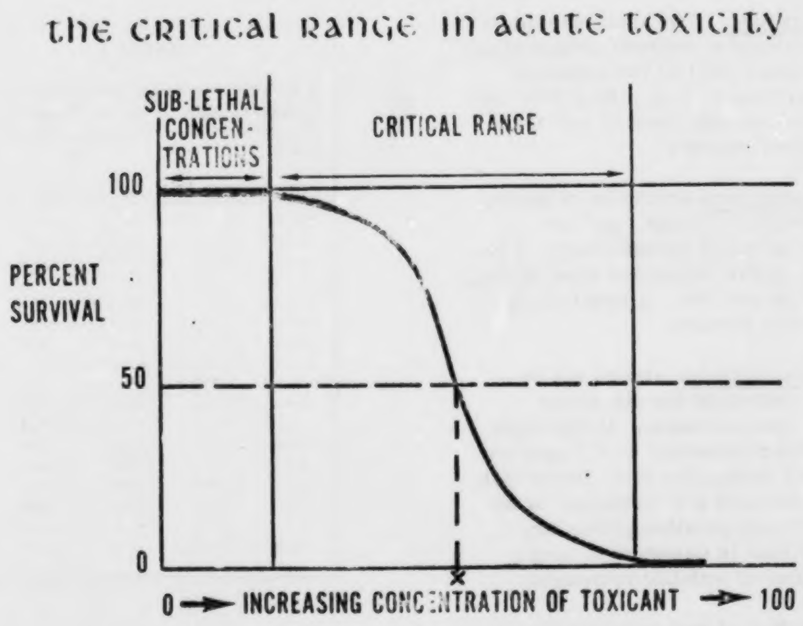

Figure 1
THE CRITICAL RANGE
X = TL50^t Concentration

1) A TL50^t is the equivalent of a median tolerance limit (TL$_m^t$).

2) This is analogous to the LC$_{50}$ (concentration survived by 50% of the population) of the toxicologist, but is more universally usable with the parameters encountered in the water environment, some of which (such as temperature) cannot be expressed as "concentrations."

3) TL50's for 96 hours or less are arbitrarily referred to as measures of "acute" toxicity, while TL50's for longer periods of time are variously referred to as sub-acute, chronic, etc.

C Special Problems of Static Tests

1 Unaerated aquaria with finite quantities of toxicant are not always satisfactory (static tests).

a The toxicant may be volatile.

b Toxic materials may be masked by a high BOD.

c The toxicant may be progressively adsorbed on container walk, fish slime, metabolized or otherwise changed so that actual concentrations in tanks change with time.

2 Standards or requirements other than those involving toxicity per se may be involved.

3 Preliminary and concurrent investigations

a Obtain all available information about unknown to be tested.

b Does the material lend itself to this type of test?

c Run feasible on the spot analyses including DO.

d Significant quantities of solutions removed from test containers for analysis should be replaced with similar volume of same dilution.

4 Wastes with a high BOD or COD

a Suggested preliminary tests:

1) Set up two identical exploratory tests.

2) Aerate one but not the other.

3) If great difference develops between them, special procedures are indicated.

b Oxygenation or aeration of dilution water before making dilutions may help.

c Renewal of solutions at stated intervals (12, 24, or 48 hours) is approved. Fish are not harmed by being carefully transferred from one container to another. It is useful where:

1) Initial DO is adequate but slowly exhausted.

2) Toxicant is volatile, progressively adsorbed, precipitated, or otherwise changed.

D Continuous Flow Procedures

1 Continuous flow procedures imply the continuous or periodic renewal of the solutions in the experimental containers, at the same time maintaining the stated concentrations (including control). The variety of devices and flow plans to accomplish this are almost infinite, two general principals will be outlined below: assaying and monitoring.

2 Continuous flow bioassay, general advantages (Figure 2)

a Materials with moderate oxygen demands may be tested.

b Materials which degrade or are volatile may be tested.

c Due to the constant removal of metabolic and other wastes, and the constant supply of fresh oxygenated water, fish may be fed and so maintained over a longer period of time. Containers must of course be maintained in reasonably clean condition.

E Test Concentrations and End Points for Continuous Flow Assays

1 Test concentrations are in general less restricted than for static tests. They need not be so high as to insure achieving the desired end point in 48 or 96 hours, although they may be so set if desired.

2 Geometric type series of concentrations are still desirable (See Table 1).

3 Sub-lethal levels may be tested over entire life histories of organisms to determine long range effects.

4 In general, the setup should be prepared, calibrated and operated for several days, or until the concentrations have become chemically and physically stabilized before introducing the fish or other experimental organisms.

F Total Fish Weight and Liquid Volume in Continuous Flow Assays

In general, the constant renewal of test solution might appear to make possible testing more or larger fish in less water. Actually, flow-through volume and total weight of fish must be so related that adequate oxygen is maintained. Furthermore, over the longer periods of time involved, "lebensraum" (or territory) must be taken into account. Organisms must not be crowded to the extent that aggressive behavior and other ecological competitive factors are introduced.

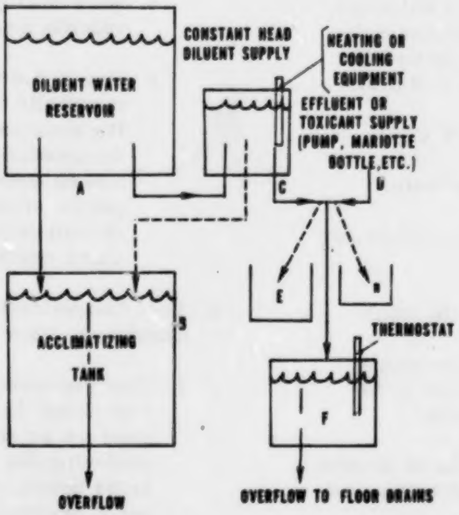
CONSTANT HEAD
DILUENT SUPPLY
HEATING OR
COOLING
EQUIPMENT
DILUENT WATER
RESERVOIR
EFFLUENT OR
TOXICANT SUPPLY
(PUMP, MARIOTTE
BOTTLE,ETC.)
A
C
D
E
n
B
THERMOSTAT
ACCLIMATIZING
TANK
F
OVERFLOW
OVERFLOW TO FLOOR DRAINS

Figure 2

BASIC SETUP FOR CONTINUOUS FLOW BIOASSAY

E to n represents one of several exposure tanks containing a graded series of dilutions of the toxicant, including one control with none.

G End Points or Reactions to be Evaluated by Continuous Flow Assays

1 The original and traditional end point of biological evaluations such as those discussed here was the death of the organism. This was simple, direct, and unequivocal. Current practice, however, often involves much more sophisticated reactions such as reduction in the reproductive capacity, or a change in the breathing rate (movement of gills).

H Special Problems of Flow Through Bioassays

1 Due to the physical requirements of maintaining stated concentrations of chemicals over long periods of time, laboratory setups are usually complicated and always require attention and maintenance.

2 The problem of disease control frequently develops in populations held over a long period of time.

3 Water and/or power failure may jeopardize an assay experiment after months of time have been expended.

4 The expense of a long continued test may not be justified by the result.

5 The above points demonstrate that in general, flow through bioassays are not adapted to day-to-day routine toxicity determinations.

III REPORTING INTERPRETATION AND APPLICATION OF BIOASSAY RESULTS

A Reporting

1 Reports should include an orderly tabulation of all pertinent data such as:

a The type of setup used and duration of test

b Identity of experimental animals

c Their source, history, average size and condition, and number used per concentration

d Source of, and chemical and physical analysis of experimental dilution water

e Experimental temperature

f Volumes of experimental liquid in each container

g Records of routine analyses such as DO and pH

h Records of chemical analyses of toxicants in experimental tanks

i $TL50^t$ or other end point, and data from which it was determined.

B Interpretation and Application

1 The $TL50^t$ is an estimate of the mid-point of the critical concentration range the interval between the highest concentration at which all test animals survive, and the lowest at which they all die (Figure 1).

2 The final step is to extrapolate from this well established mid concentration to a safe concentration well below the "critical concentration range." Extrapolating or rather: "application factors" to accomplish this are still under development and will probably not be fully developed for many years. Available data indicate that these factors must be variable according to the toxicant in question acting in combination with the receiving water in question, and considering the entire aquatic community.

3 For a more complete discussion, see FWPCA Water Quality Criteria (Reference No. 9) pp. 55-72.

4 Other considerations

a Radioactive wastes must be evaluated with regard to their chemical toxicity as well as their radioactivity.

b Sub-acute levels of many toxicants such as lead, arsenic, cadmium, etc. may exert a low level chronic toxicity over a long period of time.

c "Safe levels" of a waste in regard to toxicity to aquatic life may still exceed standards of other types such as color, organic content, suspended solids, etc.

IV BIOMONITORING AS COMPARED TO BIOASSAY (Figure 3)

A Bioassay is (as stated above) the evaluation of the effects of stated concentrations of the test material for given periods of time.

B Biomonitoring is the use of organisms to detect change in an effluent (surveillance). It operates continuously and indefinitely.

C Bioassays typically involve relatively small flows and employ often especially prepared (perhaps repeatedly prepared) batches of experimental material, while biomonitoring typically involves larger flows, from operating industries or other installations.

D Bioassays basically determine:

1 Is the substance deleterious, and if so:

2 How deleterious is it?

E Biomonitoring is useful to

1 Demonstrate the continuous suitability of an effluent (or a predetermined dilution thereof) for the survival of the test organism.

2 Detect a change (usually deleterious) in the biological acceptability of the effluent.

3 To detect a change in the effect of a mixture of the effluent and the receiving water on the test organism (i.e. to detect a change in the receiving water).

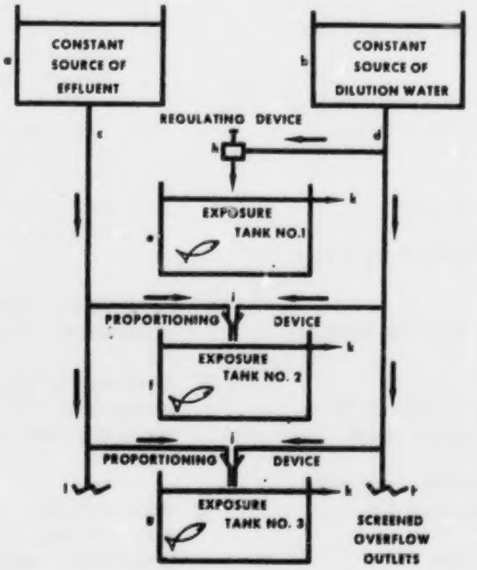
CONSTANT
SOURCE OF
EFFLUENT
a
CONSTANT
SOURCE OF
DILUTION WATER
b
REGULATING DEVICE
c
d
h
EXPOSURE
TANK NO.1
e
k
i
PROPORTIONING
DEVICE
EXPOSURE
TANK NO. 2
f
k
i
PROPORTIONING
DEVICE
l
k
l
EXPOSURE
TANK NO. 3
g
SCREENED
OVERFLOW
OUTLETS

Figure 3
BASIC SETUP FOR BIOMONITORING

F Biomonitoring was originally effective only with relatively fast acting materials, or in situations where large changes might occur rather quickly (as for example, the accidental (?) dumping of a vat of waste pickle liquor). Recent developments in the field of biotelemetry now make it feasible to "wire" a fish with electrodes (like the astronauts) and so to immediately record electronically any sudden or subtle change in the effluent which affects the physiological parameters being monitored on the live fish.

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TOXICITY IN TREATMENT PLANT PRACTICES

I INTRODUCTION

A General

An "average" sewage contains about 800 mg/1 of both suspended and dissolved solids of which about half is organic matter from humans. The organic composition amounts to about 40 percent nitrogenous, 50 percent carbohydrate, and 10 percent fats in domestic wastes.

Industry usually adds about 15 percent to the total solids load but, as is readily apparent, these contributions are more specialized depending upon location, type of industry, relative size, and activity to the collection flow.

B Treatment Practices

Good treatment practices will separate and remove the majority of the solids from the water and render it amenable for final treatment to an acceptable and inocuous effluent.

Most existing secondary treatment plants depend upon biological conversions to stabilize and to separate nutrients in the used water flow. Saprophitic organisms under favorable environmental conditions will grow to produce a slime or lacy mass of organisms and entrapped materials which can be separated from the process water. Toxic action in the treatment environment may disrupt desired conversions and result in a low quality discharge. Physical-chemical treatment operations are less sensitive to toxicity, but, it is established that carbon requirements are higher when toxicity prevails in the carbon adsorption process.

Toxicity is a real factor in cost/effectiveness of the treatment process and freedom from toxicity is also one of the major environmental quality control criteria.

Design and treatment practices for the units can be generalized only to a limited degree as influent composition and loads differ.

C Flora

Influent sewage, especially the organic component, includes large numbers of living organisms comprising practically the whole spectrum of microbiological life. In the fierce struggle for life which ensues, those forms which can better acclimate assume dominancy and serve to allow biological treatment to be a workable operation. Besides replinishing the treatment units, these living forms may function to introduce a new and necessary flora for an "exotic" new waste component which has become significant in the collection system.

An actively working flora can be disrupted by the entry of substances detrimental to their life processes and, also, improper treatment practices can suppress desirable organisms in favor of those producing a less acceptable final effluent.

II BIOLOGICAL PROCESSES

Sucessfully treated effluents are produced when an active microbial population drastically decreases or depletes the food value of the sewage and the biomass is then naturally aggregated for final removal or further treatment leaving an acceptable supernatant water for final processing. A variety of approaches are utilized to attain this final product and dependence is placed upon units with controlled environments either singularly or in combination.

A Aerobic Environment

Conditions are maintained in which dissolved oxygen is present in excess in the water mass. Microorganisms capable of surviving in this environment oxidize the sewage in the units utilizing activated or in surface active units as sand beds or trickling filters.

B Anaerobic Environment

Anaerobic degredation is characterized by a gross deficiency of dissolved oxygen. Anaerobic microorganisms are utilized in the digestion of sludge in various units.

C Environmental Control

In accomplishing these ends, the sanitary engineer designs a system which functions in a definate program. Any deviation, whether influent mediated or human error, which upsets this biological programming with an adverse effect on sewage treatment efficiency can be termed toxicity effects.

III SEWAGE TOXICANTS

Materials producing toxicity effects can be categorically listed, but, since even what can be considered as inocuous can be toxic in shock or "new type" loadings as well as the extremely large number of compounds acting in combinations as toxicants such a compomendium would be beyond the scope of this outline.

Toxicity depends on:

1. Microorganisms involved
2. Life stage of microorganisms
3. Environmental conditions at time of toxicant introduction
4. Exposure time
5. Concentration of toxicant
6. Presence of substances which can act differently in combinations
7. Solubility of toxicant
8. Adaptability of microbial flora to toxicant

A Toxicants

1. Heavy metals in the forms of salts, ions, or both.

2. Environmental shifting materials such as those effecting pH or temperature.

3. Microbiological toxicants such as those interfering with enzymatic processes.

4. Shock loaders which produce lags in processing due to an acclimation period required by the microorganisms.

B Source

This listing would also be extensive, but typical sources, by the very nature of their operations would include:

1. Metal Plating Industries
2. Refining Operations
3. Rubber, Plastic, and Chemical Industries
4. Petroleum Industries
5. Food Industry
6. Textile and Tanning Industries
7. Pharmaceutical Industry
8. Steel Industry
9. Paper Industry

C Influent Control

If status controlling the following could be effectively administered regarding sewer entry materials, toxicity from the influent waters could be minimized.

1. Temperature limitations
2. Fat, grease, and oil control
3. Substances interfering with treatment operations and control
4. pH limitations
5. Solids limitations
6. Suspended solids limitations

Of course, item 3 is the catch-all and includes a multitude of materials which vary from direct toxicants to the biological processes as well as materials which create problems regarding the human decision making as to process control.

IV EFFECTS OF TOXICANTS

Predicting the effects of a toxicant is not readily done since microorganisms do not act predictably especially when there is a tremendously large population comprising a spectrum of life forms and where some of the process specifics are still nebulous. Such mitigating circumstances as shock loadings, micribial adaption, and various combinations of substances which may be solid, dissolved, complexed, or volatile, in an active moving complex system creates an insurmountable problem. Much is known, however, about materials which can cause problems in the treatment process.

A Heavy Metals

Toxicity of these elements are well known regarding microbial life. Sewage organisms have been shown to be susceptable to nickel, copper, trivalent chromium, cadmiun, zinc, and hexavalent chromium.

A particularly distressing problem encountered with heavy metals, since they are not food sources, is a gradual buildup in treatment units until an actual stoppage of microbial action could occur if the operator is not aware of this possibility and allows, for example, an acid condition to occur in digester units increasing the more toxic soluble form of these metals.

B Acid/Alkaline Wastes

When pH is in the ranges of 6.5 to 9.5 the sewage biota can operate within acceptable limits. Within this range the bacteria are the dominant microbes as desired. With acid wastes, normally well below a pH of 5.0, a displacement could occur toward the fungal forms which show a reduced tendency to floc or clump thereby delaying or reducing treatment schedules.

Hydroxyl ions from the alkaline wastes are, again, toxic to microbial life and could cause readjustment of the preferred dominant forms, causing, as with the acid wastes, stoppage or drastically reduced treatment schedules.

With the above wastes the operator can show his mettle by either adjusting the incoming flow or the operating units by the introduction of neutralizing materials, as, for example, bubbling CO_2, a treatment byproduct, to high pH areas.

C Temperature

The "mesophilic" range (85 to 95^{o}F.) is where there is optimum biological activity. Deviations from this range as, for instance, winter climates with unheated units or heated incoming influent to treatment units will create treatment problems. Poor gasification rates or supernatants will result in poor effluents. Even a relatively minute change, as, for instance, 10^{o}F, if applied as a shock load, can effect operation.

D Other Agents

Other materials, too numerous to list, can cause operational problems. A few of these are:

Toxic Agent	Remarks
Cations: Na^+, NH_4^+, K^+, Ca^{++}, Mg^{++}	An antagonistic ion can be added to counter toxicity: Example: K^+ for Na^+ toxicity
Ammonia	Toxic as cation (NH_4^+). Avoid low pH whenever high concentration of NH_3 occurs
Cyanides	Shock loading usually disasterous. With gradual increases adaption may occur.
Mineral acids, inorganic and organic wastes	can disrupt biological system

V OPERATIONAL PRACTICES

Sewage plants are designed to protect the public health and to prevent nuisence. A skilled operator is highly desirable to operate the complex unit structure especially, as implied in this outline, where toxicity is introduced by the influent to the plant or induced by a change in operating conditions. A skilled and conscientious operator takes representative samples in key units at the proper time; keeps accurate data; and applies logic in discerning operating conditions and known remedial measures to apply where conditions deviate from the norm.

THE BASIS FOR CHLORINATION OF WASTEWATERS

I INTRODUCTION

A In a recent 1968 survey of all municipal sewage treatment plants, it was reported that an overall 30% of treatment plants were provided with facilities for introduction of chlorine in connection with treatment plant operations.

Briefly, the survey of treatment plants using chlorine may be summarized as follows:

CHLORINE USED IN TREATMENT PLANTS

Population Served	Total Number of Plants	Number Plants With Chlorination	% of Total Plants Producing Chlorination
<500	1727	323	18.7
500- 1000	2060	550	26.7
1000- 5000	4995	1903	38.1
5000- 10,000	1438	821	57.1
10,000- 25,000	1164	695	59.7
25,000- 50,000	473	318	67.2
50,000-100,000	269	187	69.5
100,000-250,000	230	170	73.9
250,000-500,000	149	97	65.1
> 500,000	73	43	58.9

B In reviewing publications relating to the use of chlorine with relation to wastewaters, the uninitiated worker quickly can gain an impression that chlorine is used in wastewater treatment operations as an almost-universal panacea, as a means of solving whatever problems seem to be plaguing the operations of the particular plant at the time.

C The purpose of this discussion is to review the common applications of chlorine to wastewaters and in the treatment of wastewaters, with special reference to the forms of chlorine that may be applied, places where chlorine may be applied, and the purposes or consequences of chlorination of wastewaters.

II USEFUL PROPERTIES OF CHLORINE

In terms of its significance in wastewater treatment processes, the important properties of chlorine include the following:

A Chlorine is a powerful oxidizing agent.

B Chlorine is poisonous to living organisms.

1 The poisonous properties of chlorine probably are exerted through its oxidizing ability, through which enzyme systems essential to life are irreversibly oxidized, or at least are inactivated.

2 According to the category of organisms for which chlorine is being used as a poison, chlorine could be called a germicide, a bactericide, a disinfecting agent, an algicide, an ovocide, a cysticide, or by any of several other "-cide" terms.

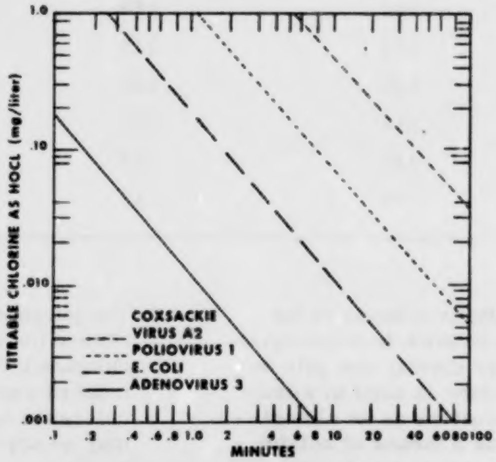
3 Different categories of organisms differ widely in their susceptibility to chlorine. Figure 1 illustrates the relative susceptibility of Escherichia coli and three different kinds of viruses, to hypochlorous acid.

4 The rate at which the disinfecting (killing) process takes place is variable, and subject to control through management of such interrelated factors as temperature, concentration, pH, and the amount, kind, and physical state of other suspended and dissolved substances present in the water.

C Chlorine is highly soluble in water, and can be introduced economically into water and wastewater with accuracy and with adequate provision to protect the health and safety of operational personnel and the population which will be exposed to contact with the chlorine-treated waters.

IV USEFUL FORMS OF CHLORINE

A Most commonly, chlorine is added to water in solution, being kept in tanks in liquid form under pressure; the liquid chlorine is converted to gas which in turn is dissolved into the water or wastewater being treated.



RELATIONSHIP BETWEEN CONCENTRATION AND TIME FOR 99% DESTRUCTION OF E.COLI AND 3 VIRUSES BY HYPOCHLOROUS ACID (HOCL) AT 0–6° C.

FROM: Butterfield, C.T.; Wattie, E.; Megregian, S. & Chambers, C.W.,[12] Clarke, N.A. & Kabler, P.W.,[15] Clarke, N.A.; Stevenson, R.E.; & Kabler, P.W.[16] and Weidenkopf, S.J.[17] Composited from Data and Figures.

FIGURE 1

B Molecular chlorine, Cl_2, in the concentrations applied, is quickly converted into other forms, characterized by the following examples:

1 Hydrolysis occurs:

$$Cl_2 + H_2O \longrightarrow HOCl + H^+ + Cl^-$$

2 Ionization of the hypochlorous acid occurs with increasing pH:

$$HOCl \rightleftharpoons H^+ + OCl^-$$

At pH 5 and lower, practically all the chlorine is in the form of hypochlorous acid; at higher pH levels, increasing ionization occurs until practically all the chlorine is in the form of the hypochlorite ion at pH 9. Hypochlorous acid is far more active chemically than the hypochlorite ion.

C Chlorine also may be added in the form of sodium or calcium hypochlorite, as chloramine, or as chlorine dioxide.

1 Hypochlorite ions enter into the same sort of equilibrium reaction in water as indicated above:

$$Ca(OCl)_2 \text{ —— } Ca^{++} + 2OCl^-$$

$$H^+ + OCl^- \rightleftharpoons HOCl$$

2 Chlorine dioxide ($Cl\,O_2$) is a gas, and is extremely active chemically and as a germicide.

3 Chloramines are formed in water containing ammonia; when chlorine is added, a mixture of monochloramine (NH_2Cl), and dichloramine ($NHCl_2$), are formed.

If enough chlorine is added to react with all the available NH_3 and still leave an excess of chlorine, then nitrogen trichloride (NCl_3) may be formed. Chloramines are less reactive chemically and less effective as germicides, than are the free forms of chlorine.

V REASONS FOR APPLYING CHLORINE TO WASTEWATERS

A Odor Control

1 If sewage becomes anaerobic, whether in the collecting system of sewers, in any unit of a wastewater treatment plant, or in a long outfall line, then unpleasant odors may be developed. These odors are due to the formation of such foul-smelling substances as hydrogen sulfide, indole, skatole, mercaptans, and cadaverin.

Hydrogen sulfide usually is regarded as the forerunner of the other foul-odor substances. Accordingly, odor-control measures are quite likely to result in control of unpleasant odors from all the substances listed.

2 Role of chlorine. Chlorine, when applied, reacts with H_2S, thus:

$$Cl_2 + H_2S \longrightarrow 2\,HCl + S$$

In addition, the addition of chlorine results in a slowing of biological activity, thereby reducing the rate at which oxygen is removed from the sewage.

3 Mode of application

a Any of the forms of chlorine indicated above may be added to sewage for odor control. However, since chlorine also reacts indiscriminately with other materials present, some workers prefer to add ferrous chloride for a more selective removal of H_2S, thus:

$$H_2S + FeCl_2 \longrightarrow FeS + 2\,HCl$$

Chlorinated benzols also have been applied in sewer systems for odor control.

b To control odors in sewer lines, chlorine is added as far up-sewer from the treatment plant as possible.

4 Chlorine treatment is highly regarded for odor control. In the concentrations used (usually 4 - 5 mg/liter, and sometimes over as wide a range as 3 - 30 mg/liter), a residual chlorine should not be produced, and treatment processes should not be impaired.

B Corrosion Control

1 Besides being an important contributor to unpleasant odors, H_2S formation can result in damage to concrete, mortar, and iron pipes. H_2S, when oxidized, results in production of sulfuric acid. Therefore, any measures taken to prevent formation of H_2S also contribute to corrosion control.

2 Dosages sufficient to prevent formation of H_2S, as above, are indicated.

C Control of Operational Problems

1 Types of operational problems

a Ponding, on trickling filters, sometimes results from formation of surface growths of organisms. These organisms partially or completely occlude the passageways for sewage through the trickling filters.

b Bulking, or failure of satisfactory settling of activated sludge, sometimes results when filamentous organisms, such as Sphaerotilus natans, and possibly other kinds of organisms, become quite prominant in the biota of activated sludge systems.

c Foaming sometimes occurs in Imhoff tanks.

d Septic, or anaerobic, conditions in various parts of a treatment plant may occur when the rate of flow or holding time in tanks or conduits is excessive and where reaeration is not provided.

2 The application of chlorine often is a useful and practical means of solving the above types of problems. The principle of chlorine application is to add a limited amount of chlorine, sufficient to inactivate or kill (selectively) the troublesome organisms, but not to sterilize the unit. In this respect, it is pointed out that there is a protection to the organisms most important in sewage treatment due to (a) the tremendous numbers of organisms present, (b) inherently greater resistance of the treatment organisms than the nuisance organisms to chlorination (debatable), and (c) treatment organisms usually are deeply embedded in a slime matrix or activated floc, and thereby are somewhat less accessible to chlorine than other forms.

D Disinfection of Sewage Effluents

1 Sewage is known to contain tremendous numbers of microorganisms of intestinal origin. When individuals harboring pathogenic organisms, whether bacteria, viruses, protozoa, and other forms of disease-causing organisms, will be present. Such organisms, when present, constitute a hazard to the health and safety of individuals coming into contact with such sewage or treatment plant effluents unless measures are taken to destroy such organisms.

a In recent years, an epidemic of infectious hepatitis was traced to shellfish harvested from polluted waters in Raritan Bay. A pollution study of some magnitude was initiated, and considerable numbers of bacteria attributable to waste treatment plants adjoining Raritan Bay were demonstrated in the study. During the period when wastewater treatment plants chlorinated the treatment plant effluents, enteric pathogenic bacteria could not be recovered. However, when chlorination of treatment plant effluents was discontinued, Salmonella were discovered with some regularity at sampling points related to the above waste treatment plant discharges.

b In studies of the Red River of the North, Salmonella has been discovered with great regularity in waters polluted through discharge of inadequately treated wastewaters. In some cases, Salmonella has been discovered where the fecal coliform count was only a few hundreds per 100 ml.

2 Chlorine functions as a disinfectant in the sense that it is applied in dosages considered sufficient to destroy the pathogenic (disease-causing) organisms. Disinfection is not construed to mean total destruction of all living organisms present in the sewage effluents (sterilization).

3 For disinfection, chlorine must be added in sufficient concentration, and with a sufficient contact time, to ensure destruction of the pathogenic bacteria.

a One basis of chlorine application for disinfection, widely noted in textbooks of sanitary engineering practices, provides recommendations for adequate disinfection by adding chlorine in an amount sufficient to kill 99.9% of all coliform bacteria in the sewage, or sewage effluent, after a contact time of 15 minutes, and to have a chlorine residual of 0.5 mg/liter (according to one recommendation, the residual chlorine should be 2 mg/liter). A widely-quoted table of chlorine application follows:

Table: Amounts of chlorine required for disinfection of sewage and sewage effluents, with chlorine residual 0.5 mg/liter after contact time of 15 minutes.

Type of Sewage or Effluent	Probable Chlorine Requirements mg/liter	Probable Chlorine Requirements lb/day/1000 persons	Chlorinator Capacities* mg/liter	Chlorinator Capacities* lb/day/1000 persons
Raw sewage, depending on strength and staleness	6 - 25	5 - 21	30	25
Settled sewage	5 - 20	4 - 17	25	20
Chemically precipitated sewage	3 - 20	3 - 17	25	20
Trickling filter effluent	3 - 20	3 - 17	25	20
Activated sludge effluent	2 - 20	2 - 17	25	20
Intermittent sand filter effluent	1 - 10	1 - 3	15	12

*For sewage flow of 100 gallons per capita per day.

b It is known that the time-concentration-temperature relationship of disinfection can be formulated in a manner analogous to demonstration of the progressive exertion of the biochemical oxygen demand. Accordingly, there has been some interest in determining amounts of chlorine to be added, based on the bacterial results to be achieved in the receiving water at some point downstream from the discharge of the treatment plant effluent.

c The attached figure, based on chlorine requirements for potability treatment of clear water, with a 30 minute contact time, are quite at variance with the requirements for producing a relatively safe effluent from a wastewater treatment plant.

E Reduction of BOD

1 It is emphasized that the action of chlorine is indiscriminate when introduced into wastewaters and treatment plant effluents. Chlorine simultaneously is killing or inactivating living organisms with which it comes into contact in sufficient concentration, for a sufficient time, and it reacts with inanimate inorganic and organic matter which also is present. In reacting with organic material, chlorine has been stated to reduce from 10% to 35% of BOD when sufficient chlorine has been added to provide a residual after 15 minutes of contact time.

2 In reducing BOD through chlorination, the action has been attributed to

a Outright chemical oxidation of the organic material,

b Combination of chlorine with organic matter to form inherently toxic compounds (such as organic chloramines), and

c Reaction of chlorine with organic matter to form chlorinated compounds which are biologically oxidized more slowly than their predecessors.

3 Chlorination of sewage for the purpose of reducing BOD is not a recommended practice, except possibly in emergencies, pending installation of adequate treatment. The principal need for chlorination for BOD reduction is to delay (and hopefully, to diffuse) the oxygen-depleting material in the receiving water to an extent such that anaerobic conditions will not develop in the aquatic environment.

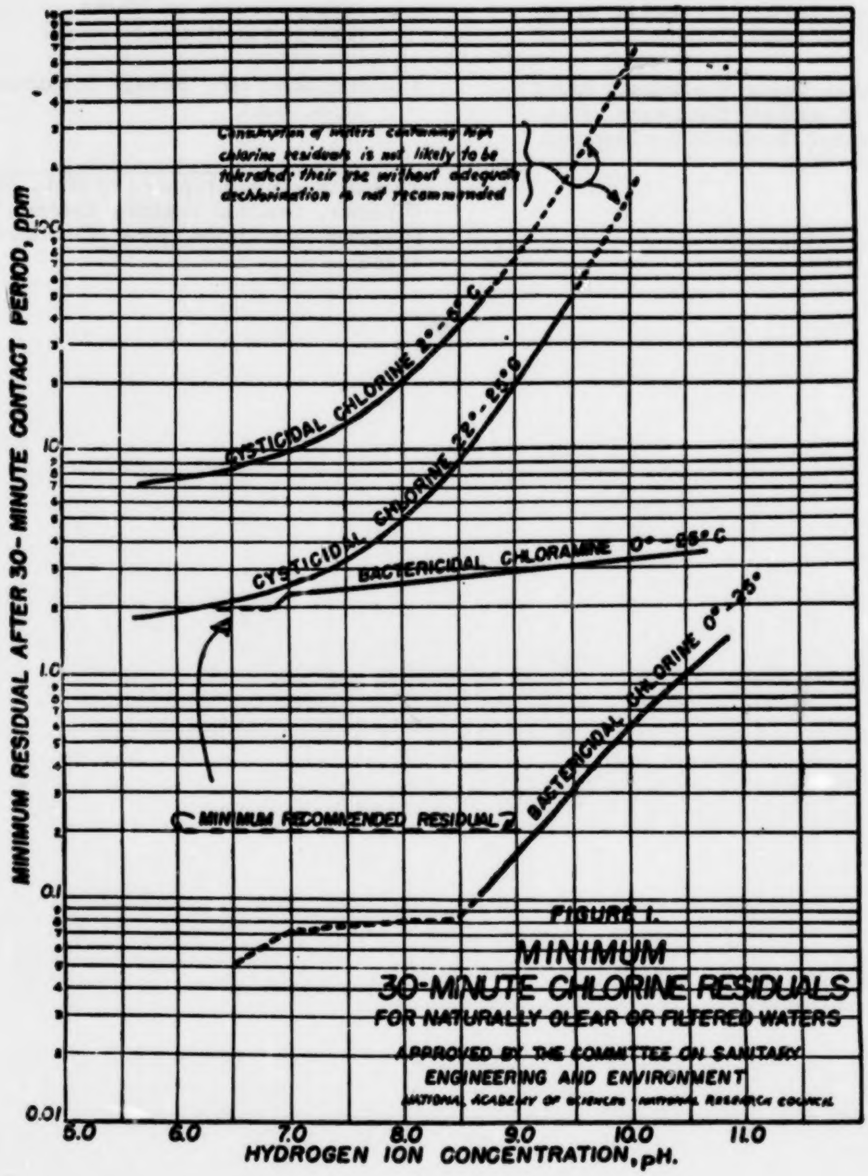


FIGURE 1.
MINIMUM
30-MINUTE CHLORINE RESIDUALS
FOR NATURALLY CLEAR OR FILTERED WATERS
APPROVED BY THE COMMITTEE ON SANITARY ENGINEERING AND ENVIRONMENT
NATIONAL ACADEMY OF SCIENCES - NATIONAL RESEARCH COUNCIL

REFERENCES

1 The Federation of Sewage and Industrial Wastes Association. Sewage Treatment Plant Design. 1959.

2 Great-Lakes-Upper Mississippi River Board of Sanitary Engineers. Recommended Standards for Sewage Works. 1960.

3 Cosens, Kenneth W. The Operation of Sewage Treatment Plants. A reprint from Public Works Magazine.

4 Imhoff and Fair. Sewage Treatment. 1956, Book.

This outline was prepared by H. L. Jeter, Director, National Training Center, Water Program Operations, EPA, Cincinnati, OH 45268.

WASTEWATER TREATMENT: SCHEMATICS, FUNCTIONS, AND OPTIONS

I INTRODUCTION

A Wastewater treatment facilities are engineered to recondition used water for beneficial reuse. Traditionally these facilities are designed to achieve in a shorter time and smaller space a similar degree of self purification that may occur naturally under low load conditions. Increasing loading and increasing water rinse requirements means that both design and operation of treatment plants be upgraded to improve cost effectiveness in general and specific cleanup.

B Increasing population concentration and activity have caused increased stress on treatment to meet Water Quality Standards established by state, regional and federal authority for the Nation's water resources. These are dynamic standards subject to adjustment with the changing needs of the situation. This adjustment may be expected to require higher and higher treatment efficiency for more items.

1 Effluent quality or discharge limits are receiving increasing stress to implement Water Quality Standards.

2 General treatment criteria such as BOD, suspended solids, and coliform group organisms are being supplemented by additional items such as phosphorus, nitrogen, mercury, fecal coliform, and other more specific discharge limitations.

C It is technically possible to recondition used water for any reuse purpose. Economics, public apathy, opinions, operational competence, enthusiasm, and enforcement commonly limit what will be done in a given situation.

1 Conventional wastewater treatment presupposes municipal wastewater treatment generally. Inclusion of wastewaters from industrial operations making specialty products designed to be more resistant to decay, more physiologically effective, or more potent for some intended use frequently have adverse effects upon biological treatment. Further, specialty wastewaters tend to be more concentrated point source discharges that accentuate treatment problems.

2 Certain wastewater components tend to be much more difficult to remove than others because of availability, recycle, interference during treatment, etc. Special procedures may be required to meet acceptable effluent requirements when these are encountered.

3 Cost of treatment tends to increase rapidly as effluent quality criteria rise. It may be possible to remove 90% of the influent concentration at a cost of about $0.20/1,000 gallon (lower costs tend to be associated with higher influent concentrations). Upgrading to 95 to 99% removal may result in a cost increase larger than that to obtain the first 90% removal. Processes, techniques, and equipment improvements are likely to be required.

D The following schematics present an overview of what may be found in a wastewater treatment plant and the functional purpose of various items. These are not intended to be complete or detailed. Other sources of information provide details.

1 It is not possible to generalize what shall be included in a given plant. The state agency or agencies designated for water quality responsibility have primary interest. Planning agencies involved designate Water Quality Standards and/or Effluent criteria requirements in accordance with Statutory authority and regulations. Local, state, and federal authorities regulate how the financial arrangements will be handled and the financial limitations of the projects for design, construction and operation.

2 Plant design is the responsibility of a professional consultant who is designated to select the hardware and processes to meet the needs of the situation as defined by planning agencies. Information gathered from the record, current and projected activities of the distributing population, nature of the wastewater load, quality requirements of the receiving water, availability of water, site survey, treatment, experience or studies all contribute to design consideration.

3 The designed plant does not become a functional reality until construction and operation has been financed with people competent to do the job. "Too little-too late" is a common problem in treatment facilities because of losses in transit and/or the fact that needs grow faster than available facilities and manpower.

E Options in treatment technology must be qualified. There are many alternate routes for achieving a given treatment objective. They are not equals with respect to cost, time, space, performance, operation, opinion, etc.

1 Local opinion often favors one treatment option over another that is considered better in terms of cost efficiency and dependability by another area and another group.

2 Relative cost for land, hardware, and operation are a large factor in process selection.

3 Established practice, good or indifferent tends to perpetuate itself. It is much less effort to "sell" a well known process than to design one precisely fitted to the situation.

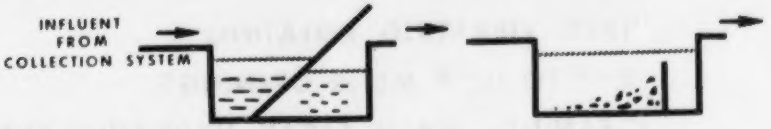
This outline was prepared by F. J. Ludzack, Chemist, National Training Center, Water Program Operations, Environmental Protection Agency, Cincinnati, OH 45268.

The following schematics and options are for orientation purposes only. They are not intended to illustrate all possible treatment schemes or any one treatment plant. Implications of preference are not to be assumed by inclusion, omission, or order of appearance.

Nineteen illustrations to follow

WASTE WATER TREATMENT SCHEMATICS
PRE-TREATMENT

COARSE SCREENS 1 TO 5 IN. SPACING	GRIT CHAMBER



TO REMOVE:	TO REMOVE:
ROCKS	SAND
ROOTS	GRAVEL
RAGS	HIGH DENSITY ITEMS
OTHER LARGE ITEMS	

TO PROTECT SUBSEQUENT PROCESS EQUIPMENT AND OPERATIONS

WASTEWATER TREATMENT OPTIONS
COARSE SCREENING

MANUALLY OR MECHANICALLY CLEANED: FIXED OR MOVING RAKES: CLEANING CYCLE ACTUATED BY :

- **TIME**
- **OPERATOR**
- **PRESSURE OR LEVEL CONTROL**

SCREENINGS DISPOSAL

- **BURIAL**
- **DRYING & INCINERATION**
- **GRINDING & RETURN TO PROCESS WATER**

FINE SCREENING OR MICROSTRAINING

PROCESS STAGE:

PRE- POST- OR CONTINGENCY TREATMENT

OPTIONS:

WEDGE WIRE, WIRE CLOTH,
CYLINDER, PLATFORM
FIXED, VIBRATING, ROTATING
10^{-4} TO 10^{-8} METER OPENINGS
CLEANING: WATER SPRAY, HYDRAULIC SHEAR

TO REMOVE:

FIBER, STRINGS, PLASTICS, FLOC
AGGLOMERATES, MISC. PARTICLES,

WASTEWATER TREATMENT OPTIONS
GRIT REMOVAL

LOCATION

- COLLECTION SYSTEM
- PLANT HEADWORKS
- IN PROCESS

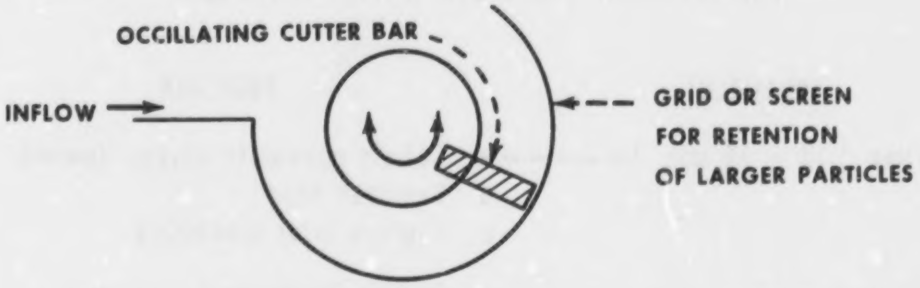
TYPES OF EQUIPMENT

- LONG NARROW CHANNELS (HORIZONTAL FLOW)
- CIRCULAR FLOW BASINS (CYCLONES)
- UPFLOW TYPE BASINS
- CENTRIFUGE EQUIPMENT
- MANUAL OR MECHANICAL GRIT REMOVAL (SOME TYPES)
- HYDRAULIC GRIT WASHING

GRIT DISPOSAL

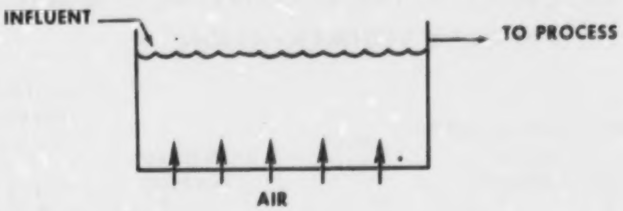
- BURIAL
- FILL (OF WASHED MATERIAL)

WASTEWATER TREATMENT SCHEMATICS COMMINUTION


OCCILLATING CUTTER BAR
INFLOW
GRID OR SCREEN
FOR RETENTION
OF LARGER PARTICLES

TO REDUCE SIZE OF WATER CARRIED MATERIALS ENTERING SUBSEQUENT PROSSESS UNITS
MAY INVOLVE CUTTING, GRINDING, SHREDDING, CRUSHING, HAMMERING, ETC.
MAY INCLUDE TAKEOUT OF SELECTED MATERIALS

PREAERATION


INFLUENT
TO PROCESS
AIR

LOCATION:
- PLANT HEADWORKS
- COLLECTION SYSTEM
- PROCESS DISTRIBUTION CHANNELS

OPTIONS:
- 10 - 30 MINUTES
- AIR OR OXYGEN
- TANKS, U TUBES, PRESSURE PIPES OR CHAMBERS
- TO PREVENT SEPSIS ODOR CONTROL, IMPROVE LATER TREATMENT, REDUCE O_2 REQUIREMENTS

WASTEWATER TREATMENT OPTIONS

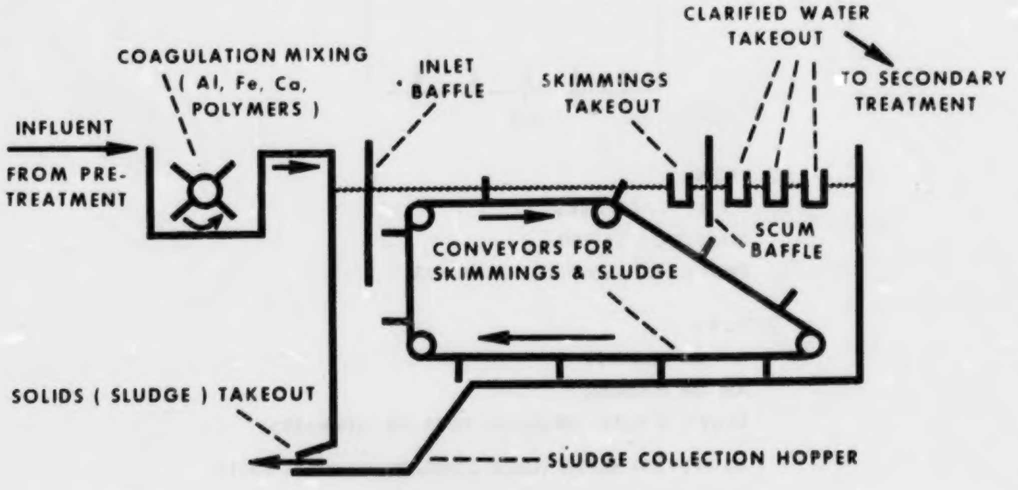
PRE-AERATION, PRE-CHLORINATION, OZONATION

TREATMENT — **FUNCTION**

1. Aeration (10 – 30 min.) ----- a. Satisfy immediate oxygen demand
   b. Decrease odor
   c. Improve later processing
2. Chlorination ---------------- Partial disinfection + group 1
3. Ozonation ----------------- Decrease odor primarily + group 1 & 2
4. Pressurized Aeration & Release -----Floatation of grease, oil, solids
   May pressurize part or all of the flow
5. Additional Degritting during retention

WASTEWATER TREATMENT SCHEMATICS

PRIMARY SEDIMENTATION

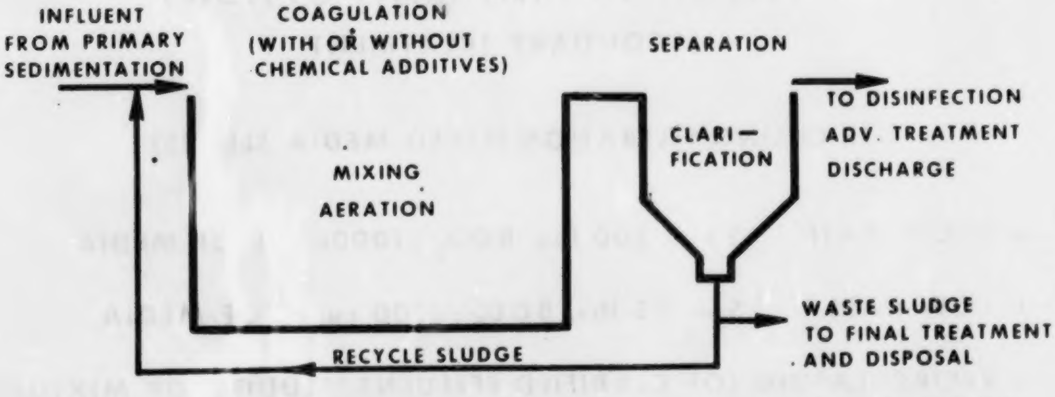

CLARIFIED WATER TAKEOUT
TO SECONDARY TREATMENT
COAGULATION MIXING (Al, Fe, Ca, POLYMERS)
INLET BAFFLE
SKIMMINGS TAKEOUT
INFLUENT FROM PRE-TREATMENT
SCUM BAFFLE
CONVEYORS FOR SKIMMINGS & SLUDGE
SOLIDS (SLUDGE) TAKEOUT
SLUDGE COLLECTION HOPPER

FUNCTION: TO SEPERATE FLOATABLE OR SETTLEABLE SOLIDS FROM THE CLARIFIED PRODUCT WATER

PRIMARY SEDIMENTATION OPTIONS

1. MAY BE OMITTED FOR CERTAIN SECONDARY TREATMENT OPTIONS
2. MAY OR MAY NOT INCLUDE COAGULATION
3. VARIOUS TANK ARRANGEMENTS: RECTANGULAR
   OR CIRCULAR TANKS SLUDGE TAKEOUT AT
   INLET OR OUTLET POSITIONS
   PLOW OR SUCTION SLUDGE COLLECTION
   CIRCULAR OR GRID OVERFLOW WIERS

WASTEWATER TREATMENT SCHEMATICS
SECONDARY TREATMENT


INFLUENT FROM PRIMARY SEDIMENTATION
COAGULATION (WITH OR WITHOUT CHEMICAL ADDITIVES)
SEPARATION
TO DISINFECTION
ADV. TREATMENT
DISCHARGE
CLARI- FICATION
MIXING
AERATION
WASTE SLUDGE TO FINAL TREATMENT AND DISPOSAL
RECYCLE SLUDGE

FUNCTION: LIQUID TO SOLIDS TRANSFER
BIO- AND/OR CHEMICAL FLOCCULATION
PARTIAL OXIDATION
CONVERSION OF SOLUBLE & COLLOIDAL SOLIDS TO SEPARABLE FORM

SEPARATION OF CLARIFIED PRODUCT WATER FROM SKIMMINGS OR SLUDGE

WASTEWATER TREATMENT OPTIONS

SECONDARY TREATMENT

1 ACTIVATED SLUDGE (FLUID SLIME SUSPENSION)

a HIGH RATE > 1.0 lb. COD/ lb. MLVSS/DAY

b CONVENTIONAL 0.4 – 1.0 lb. COD/MLVSS/DAY

c EXTENDED AERATION < 0.4 lb. COD/lb. MLVSS/DAY

d COMPLETE MIX OR PLUG FLOW

e MECHANICAL, DIFFUSED AIR OR COMBINATION OXYGENATION

f CONTACT, 2 STAGE, TAPERED AERATION, STEP FEED, KRAUSE PROCESS, CHEMICAL COAGULATION, N_2 OXID.-RED.

WASTEWATER TREATMENT OPTIONS

SECONDARY TREATMENT

TRICKLING FILTRATION (FIXED MEDIA SLIMES)

a HIGH RATE 25 – 300 lbs. BOD_5 /1000cu. ft. OF MEDIA

b LOW RATE 5 – 25 lbs. BOD_5 /1000 cu. ft. OF MEDIA

c RECIRCULATING (OF CLARIFIED EFFLUENT, SLUDGE, OR MIXTURES)

d SHALLOW OR DEEP BEDS

e ROCK, SLAG, OR MANUFACTURED MEDIA

f 2-STAGE, NATURAL OR FORCED DRAFT, COMBINED TRICKLING FILTRATION AND ACTIVATED SLUDGE

WASTEWATER TREATMENT OPTIONS

SECONDARY TREATMENT

OXIDATION PONDS

A DEPTH : SHALLOW (1 - 5 FT) DEEP (5 - 25 FT)

B TIME:

$<$ 3 DAYS PRIMARILY SEDIMENTATION
3 - 20 DAYS SUSPENDED SLIME GROWTH
$>$ 20 DAYS GROWTH FLOCCULATION, DEPOSITION

C SINGLE OR MULTIPLE PONDS
SERIES OR PARALLEL OPERATION

D PRIMARILY AEROBIC, ANAEROBIC, FACULTATIVE

E NATURAL OR FORCED AERATION & MIXING

F RECIRCULATION (EFFLUENT, SOLIDS, OR MIXTURES)

G LEVEL CONTROL :(OVERFLOW, PERCOLATION, EVAPORATION)

H CLARIFICATION: INCIDENTAL OR SEPARATE
ENGINEERED OR NATURAL SOLIDS TAKEOUT

WASTEWATER TREATMENT OPTIONS

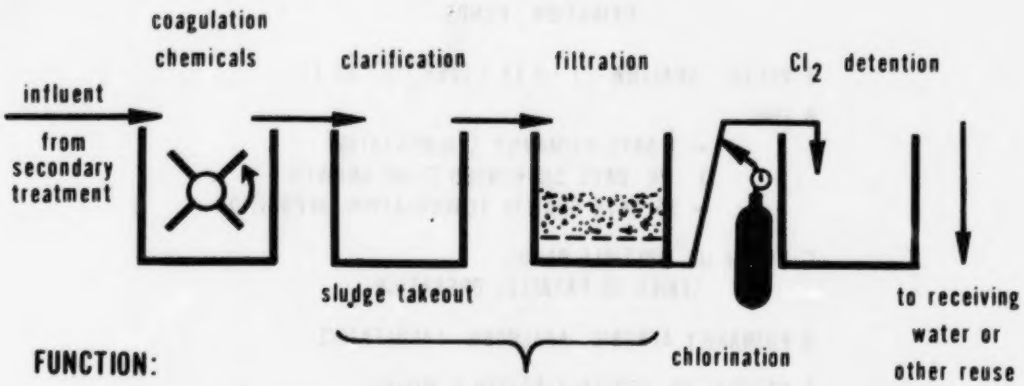
PHYSICAL - CHEMICAL TREATMENT

1. APPLICATIONS
   A. RAW WASTEWATER
   B. IN PROCESS SUPPLEMENTATION TO BIOL. TREATMENT
   C. AFTER BIOLOGICAL TREATMENT

2 NATURE OF TREATMENT
   A. LIME COAGULATION
   B. ALUM OR IRON COAGULATION
   C. POLYMER COAGULATION
   D. AMMONIA STRIPPING
   E. CARBON ADSORPTION POWDER OR GRANULAR
   F. FILTRATION : (SAND, MIXED BED, SOIL MICROSTRAINING MOVING BED)
   G. ELECTROPHORESIS
   H. ION EXCHANGE
   I. DISTILLATION
   J. DISINFECTION
   K. CHEMICAL OXIDATION

WASTEWATER TREATMENT SCHEMATICS

TREATED LIQUID STREAM


coagulation chemicals
clarification
filtration
Cl_2
detention
influent
from secondary treatment
sludge takeout
chlorination
to receiving water or other reuse

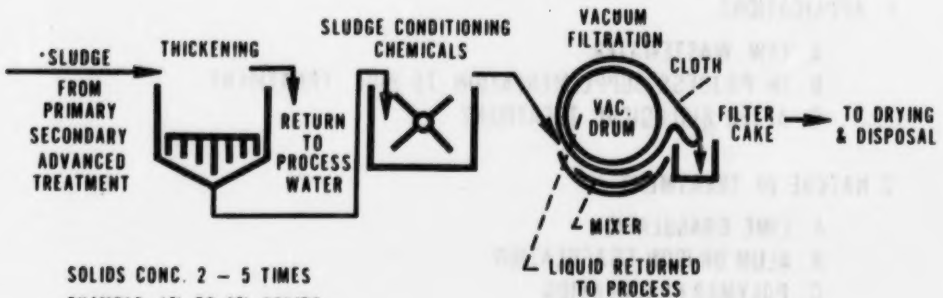
FUNCTION:

TO INCREASE POSSIBILITIES FOR REMOVAL OF ITEMS PASSING THROUGH CONVENTIONAL TREATMENT

TO PRODUCE A WATER LOW IN DISSOLVED OR SUSPENDED SOLIDS (BIOLOGICAL OR OTHER)

TO DISINFECT THE DISCHARGE

WASTEWATER TREATMENT SLUDGE DEWATERING


SLUDGE
FROM PRIMARY SECONDARY ADVANCED TREATMENT
THICKENING
RETURN TO PROCESS WATER
SLUDGE CONDITIONING CHEMICALS
VACUUM FILTRATION
CLOTH
VAC. DRUM
FILTER CAKE
TO DRYING & DISPOSAL
MIXER
LIQUID RETURNED TO PROCESS

SOLIDS CONC. 2 – 5 TIMES
EXAMPLE: 1% TO 4% SOLIDS

SOLIDS CONC. 5 TO 10 TIMES
EXAMPLE: 4% – 25% SOLIDS

FUNCTION:

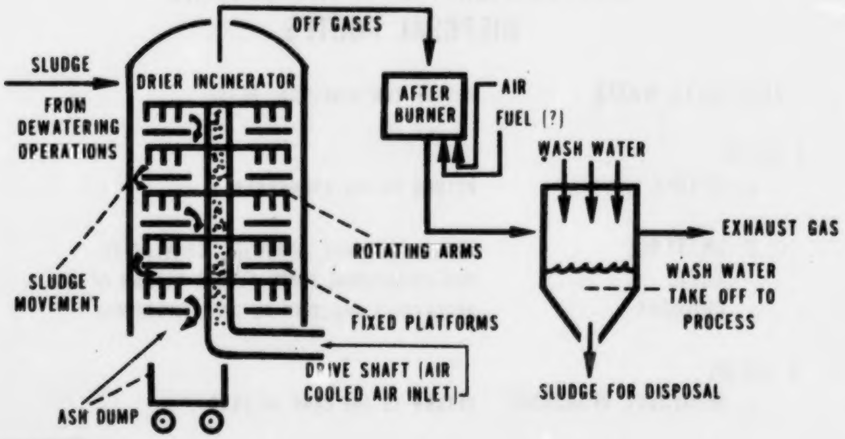
To reduce the water content of the sludge as much as possible by the most economical and feasible route for the situation.

To reduce the amount of water to be evaporated.

WASTEWATER TREATMENT OPTIONS
SLUDGE DEWATERING

1 LAND SPREADING (COVER CROP, TILLING, BURIAL)
2 SLUDGE DRYING BEDS
3 FILTRATION (VACUUM, VIBRATING SCREENS, SAND, ETC.)
4 INDUCED HEAT (SPRAY, ROTARY KILN, TRAY)
5 CENTRIFUGATION
6 FREEZING
7 CHEMICAL CONDITIONING
8 HIGH PRESSURE & TEMPERATURE DIGESTION
9 FLOTATION
10 SEDIMENTATION

WASTE WATER TREATMENT SCHEMATICS
SLUDGE DRYING & DISPOSAL


OFF GASES
SLUDGE
FROM DEWATERING OPERATIONS
DRIER INCINERATOR
AFTER BURNER
AIR
FUEL (?)
WASH WATER
EXHAUST GAS
ROTATING ARMS
SLUDGE MOVEMENT
WASH WATER TAKE OFF TO PROCESS
FIXED PLATFORMS
DRIVE SHAFT (AIR COOLED AIR INLET)
SLUDGE FOR DISPOSAL
ASH DUMP

FUNCTION:

To complete the drying operation and convert intermediate products to their highest oxidation state.

To stabilize off gases with respect to odor, oxidation state, and suspended solids.

WASTEWATER TREATMENT OPTIONS
SOLIDS DISPOSAL METHODS

1 LAND DISPOSAL: FOR REUSE, CROPPING, SOIL CONDITIONING, FOR ISOLATION, SANITARY FILL

2 INCINERATION: FOR CONVERSION TO INNOCUOUS GASES & ASH AT THEIR HIGHEST OXIDATION STATES

3 TRANSPORT TO REMOTE AREAS

4 SEA DISPOSAL: PREFERABLY DEEP WATERS

5 RECOVERY FOR REUSE

6 UNDERGROUND INJECTION

WASTEWATER TREATMENT OPTIONS
DISPOSAL ROUTES

1 RENOVATED WATER	RETURN FOR BENEFICIAL REUSE
2 GASES	
a. STABLE	RETURN TO THE ATMOSPHERE
b. UNSTABLE TOXIC ODOROUS	OXIDIZE, RECOVER, STABILIZE, CONVERT TO NON-POLLUTIONAL FORM, BEFORE RETURN OF THE ACCEPTABLE FRACTION TO THE ATMOSPHERE
3 SOLIDS	
a. INSOLUBLE INORGANIC	RETURN TO THE LAND OR SEAS
b. SOLUBLE INORGANIC	RETURN TO SALINE WATERS, ISOLATED SALINE SUBSURFACE STRATA, RECOVER FOR REUSE
c. ORGANIC	STABILIZE, CONVERT TO GASES ACCEPTABLE FOR RETURN TO THE AIR AND SOLIDS ACCEPTABLE FOR RETURN TO THE LAND, ISOLATE SOLIDS WITH MINIMUM WATER CONTACT

BEHAVIOR OF SPECIFIC CHEMICAL COMPOUNDS IN THE AQUATIC ENVIRONMENT

I INTRODUCTION

A Discharge of specific chemicals to water may have a variety of effects such as:

1 Oxygen demand

2 Plant nutrition

3 Infection

4 Toxicity

5 Sedimentation

6 Radioactivity

7 Other mineral and organic effects (pH, color, oil, etc.)

8 Heat

This is one classification modified slightly from that used by Eisenhaur[1] which is primarily health-related. Other classifications by effect, by industry, by biological, chemical or physical attributes take a variety of forms.

B A given chemical is likely to be associated with several effects.

1 Oxygen demand may be chemical, biological, or both. Cell mass production, associated with oxidation, results in sediments, plant nutrients, pH effects, etc.

2 Infectious materials commonly are not associated with chemical discharges, but may be as a result of association with infected personnel, pharmaceutical testing, etc.

3 Heated discharges are associated with specific chemicals to the extent governed by process water technology and subsequent treatment. Heat and pressure are common reaction controls in chemical manufacturing or processing.

4 Toxicity is an action induced by too much of any component (exceeding biological tolerance). Toxic agents of common interest are those that exert toxicity at low concentrations.

C Evaluation of Behavior

1 Cursory examination is likely to suggest obvious behavior characteristics on the basis of past experience or short time observation.

2 New or troublesome chemical components may require long-term systematic investigation as outlined[2] to identify unusual behavior that may become associated with major problems in subsequent reuse of the contaminated water.

3 High rate exertion of some behavior aspect is readily apparent. The investigator must guard against low rate effects that do not become apparent except over a long period of time or when gross quantities are involved. There are no "undegradable" materials.

II NATURE OF POSSIBLE CHEMICAL EFFECTS

A Biological effects associated with specific chemicals depend upon whether the chemical may enter the metabolic pathway as a nutrient, interfere with life processes, or coexist with little apparent interaction.

1 Each chemical may stimulate respiration, support it, or become bacteriostatic or germicidal,

depending upon concentration and organism tolerance for that particular chemical and species. Some low concentration commonly stimulates, but each chemical has some concentration at which it is deleterious to metabolism. A pesticide may have all three ranges compressed into the microgram/liter range; sugars may require 20 to 30% concentrations to be inhibitive.

2 A given chemical may be readily available for metabolic reactions or it may react too slowly to be observable except on a long-term basis.

3 Certain chemicals may enter metabolic pathways via common enzyme systems characteristic of many organisms. Others may require selected organisms capable of producing special adaptive enzymes.

4 Certain chemicals may be toxic as a result of destruction of the reversible characteristics of enzyme systems. Malfunction of nerve tissue activity, or interference with some other vial function.

5 A chemical that has little apparent reactability in all mass may thicken cell walls and/or alter transport characteristics across the membrane, may inhibit availability of other essential nutrients by substitution or dilution, and by habitat covering.

B Chemical Effects

1 Acid or alkaline chemicals in excess of the natural buffer capacity of the water affect water quality by making it unsuitable for life processes, irritating, corrosive, or otherwise damaging.

2 Reactive chemicals in water solution may cause formation of precipitates, redissolve boundary deposits, cause formation of undesirable odors, color or taste, and reaction or complexation products of essential materials into a form less desirable or less acceptable for beneficial reuse.

3 Specific chemicals may be manufactured for a specific purpose such as pharmaceuticals, pesticides, growth-controlling hormones, dispersing action, or for stability of response as a protective coating, color, textile, elastomer, container, etc. Mixtures of these and other items in wastewater are not subject to behavior generalities. Behavior is a function of the particular substance and situation.

4 Reactability is a function of the net energy change resulting from the conversion of reactants to products. Those reactions associated with a large net energy release are favored in chemical and biological stabilization. Low net energy yields favor low rate processes.

C Physical Effects

Size, solubility, contact, temperature and pressure largely control favorability among the possible biological or chemical reactions.

1 Aggregate or molecular size controls surface area per unit mass which in turn controls contact possibilities. Large sizes limit reactability. Physical barriers to penetration into the mass or product migration away from the interior are a function of porocity, shape, mass, type and thickness of the material.

2 Rapid reactions are more likely among soluble materials, providing energy release and turbulence are comparable. Equilibrium conditions are shifted toward reaction completion if one or more products are insoluble or otherwise less available.

3 Contact or mixing characteristics determine the probability with which one reacting substance is likely to

enter the reacting zone of another. Air contains abundant oxygen, surface water is likely to approach saturation values for DO. It is rare to encounter adequate oxygen in the vicinity of benthic deposits without vertical mixing.

4 Temperature affects rate of reaction via several mechanisms. A rise of 10° C approximately doubles reaction speed as a result of increased solubility, molecular motion, fluidity, ionization, etc. Increased temperature may have the opposite effect if density stratification decreases mixing or the chemical doesn't follow the trends listed in the preceding sentence.

5 Pressure may promote contact of certain materials but if a gas happens to be a reaction product, increased pressure decreases or changes the course of likely reactions. Increased compaction of sediments is likely to decrease availability for interaction.

6 Changes in physical state form a gas or liquid to solid limits contact to interface zones. Gases of limited water solubility and liquids that are immiscible with water also decrease availability.

III MAJOR EFFECTS OF SELECTED CHEMICALS IN WATER (3, 4, 5)

A Mineral Oil

1 May be discharged in liquid or emulsified form. It is commonly entrapped by cell mass or other particulates to form scum, oily sludge or boundary deposits.

2 Biodegrades slowly at temperatures over 10° C, in concentrations below 10 mg/l under aerobic conditions. Little action anaerobically.

3 Tends to have a deleterious effect upon the biota, produces objectionable tastes, odors, boundary deposits. Covers the bottom with an oily "goop."

B Phenolics

1 Monohydroxy benzene (phenol) is one of the most rapidly biodegraded chemicals known for adapted cultures and concentrations below about 50 mg/l. Noted for oxygen demand.

2 Phenolics tend to produce objectionable odors particularly upon partial chlorination, but may be destroyed by more complete chlorination.

3 Substituted phenolics range from readily degradable to highly toxic or resistant chemicals.

4 Toxic at high concentrations. Tends to break down cell membranes.

C Carbohydrates

This group represents an homologous series ranging from low to high molecular weight components with reactability decreasing as molecular weight increases.

1 The low molecular weight carbohydrates (sugars) are the primary compounds of the food chain and for respiratory energy dynamics. Higher homologues must be hydrolyzed to enter the food chain.

2 Carbohydrates favor rapid cell mass production providing sufficient other nutrients are available to form proteins. Nitrogen and phosphorus are most commonly limiting but other essentials such as growth factors, minerals, etc., may be needed.

3 Prolific slime growth, frequently filamentous, is encouraged by available carbohydrates. Oxygen demand and solids problems are major difficulties.

D Organic Acids

Organic acids, such as acetic, are transitory products of protein hydrolysis and deamination. They may be used in resynthesis or readily oxidized to CO_2 and water. Anaerobic destruction results in CO_2 and CH_4.

1 The discharge of significant organic acids or acid-producing components such as milk commonly leads to low pH problems as a result of the acid release and CO_2 produced from oxidation or rearrangement.

2 Organic acids of low molecular weight are readily available for biochemical transformation with acid reactions produced early, alkaline products in later stages. Feedback of later stage oxidation products favors control of pH and process dynamics.

3 Organic acids such as acetic acid are one step removed from the highest attainable stage of oxidation. They contain a major fraction of total oxygen requirements, hence oxygen demand is a function of the quantity of material rather than oxygen requirements per mole. Stabilization favors oxidation and rearrangement to a greater extent than resynthesis.

4 Higher homologues of the series show decreasing availability and pH effects.

E Amines

Amines are a common product of proteolysis (protein hydrolysis); deamination results in formation of organic acids and ammonia. The amino acid series includes many items essential to protein and enzyme synthesis. Mixed organisms are likely to be capable of synthesizing necessary amines from the mineral components but one specie is unlikely to have the capacity to synthesize all of the required amino acids. Availability from preformed sources decreases the need for synthesis.

1 Amine compounds are among those contributing objectionable odor characteristics when present in significant amounts in water (putrid odors).

2 Stabilization dynamics favor deamination of excessive amines to produce acids and ammonia. Carbon hydrogen and nitrogen oxygen demand may be very high in degrading fractions while solids problems and oxygen demand are characteristic [illegible] growing systems.

3 High reactability of primary amines encourages high rate conversions. Secondary and tertiary amines show decreased reactability.

F Pesticides take a variety of forms, all of which are intended to disrupt metabolic processes. They may be highly persistent such as DDT and Chlordane, or readily hydrolyzed such as certain phosphorus and carbamate products. Distribution and persistence are major factors pertinent to behavior in water.

1 Organic pesticides are likely to be more soluble in oily materials than in water. They tend to become distributed accordingly. It is common to find very high concentrations of the pesticide in or on cell mass, organic residues, oily materials or surface films, or on other active surfaces such as silt.

2 Pesticides seem to be selective in the degree of effect among organisms. Slime organisms tend to concentrate organic pesticides to a high degree but have a high tolerance factor. Certain organisms such as fish are highly sensitive and tend to be the victims of pesticide concentration through the food chain as well as by other contact.

3 Pesticide concentrates in bed loads, boundary deposits, living organisms and ducts tend to be transported widely by motility, air or water carriage unless the compound is subject to natural degradation to innocuous products.

G Detergents - Surfactants

A detergent is a cleaning agent consisting of a surfactant (surface active agent) and various items added in process, builders to aid detergency, and special additions added for sales appeal, shelf storage, or usability.

1 Detergents are unique among manufactured products -- essentially all of that used is discharged in the carriage water along with the removed contaminants of the cleansed items.

2 Surfactants are intended to reduce surface tension. Cell membranes are characterized by certain surface active properties which may be altered by surfactants.

3 Most treatment operations tend to promote agglomeration and/or oxidation. A detergent generally contains dispersing agents which complicate treatment technology.

4 Detergent production has been modified to improve treatability. Treatment plant capacity and control need upgrading in line with the load and situation.

H Coloring Agents - Dyes

Organic coloring agents include many complex agents designed to produce a color effect that is resistant to changes induced by light, heat, chemicals and time. The variety of chemicals used causes shifts in behavior and applicable means of treatment.

1 Color is the primary problem. Its removal usually requires physical-chemical treatment because dyes are likely to be inhibitive to organisms, and are not readily removed in process. Storage tends to equalize colors and blend them into a conglomerate amber hue with some removal in process.

2 Acid or alkaline agents are commonly used to "fix" the colors. It is unlikely that coloring operations will result in acid/base equivalency without additional neutralization.

I Inorganic Salts

Chlorides or sulfates may be added to water as a result of domestic use water treatment, manufacturing, mining, or many other operations.

1 Sodium potassium or other monovalent cations tend to produce soluble salts that may interfere with beneficial uses of water as a result of taste, osmotic pressure changes, cathartic action or other effects. Soluble mineral salts commonly are inefficiently removed during conventional treatment. Distillation electrophoresis reverse osmosis, freeze-out, and certain other procedures are more feasible.

2 Certain multivalent action sulfates are relatively insoluble and may be precipitated. Chlorides generally are quite soluble. The cation may be converted to insoluble carbonates, but any substitution reaction is likely to produce soluble components similar to those in I-1 that limits total dissolved solids removal.

3 Deposited material frequently may be redissolved under favorable conditions. That which remains tends to fill the deposit area and make it less desirable for aquatic growth or beneficial reuse.

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Methods given are examples of possible routes to the test criteria sought. Background material on interferences and possible problems are considered in an effort to enhance probabilities for meaningful test results.

USEPA Analytical Quality Control Methods are featured. Other tests are described such as those used for preliminary information or process control where test simplicity and rapid information recovery are important.

Official status is not intended. Authorities of jurisdiction for an area or situation establish official methods.

SAMPLING IN WASTEWATER TREATMENT OPERATIONS

I INTRODUCTION

A A sample is defined as a representative part, aliquot or single item from a larger group or whole to be presented for inspection or testing for quality; also, a portion of a statistical population whose characteristics are studied to gain information about the whole.

B A sample representing materials at a given time, place and flow may be called a "catch" or "grab" sample. A series of grab samples obtained over a specified period of time from the sample flow becomes a "composite" sample when all individual samples are combined into one. If the individual grab sample volumes are adjusted in proportion to flow at the time they were obtained and before combining them the resulting mixture is a "proportional composite."

C Sampling requires careful observance of procedures to be meaningful:

1 The scale up factor from the sample to the whole commonly is very large. Behavior of a 1 ml sample of the incoming flow in a BOD dilution may be used to estimate loading; a 0.001 ml sample may be used for estimation of membrane filter coliform group organisms for many million gallons of flow.

2 The sampler is obligated to insure that his sample does represent the material sampled and is protected from inadvertent changes. Proper attention to detail and identification is imperative.

3 Grab samples of flow into and out of process are likely to give misleading information if process detention time has been ignored. If both are obtained at about the same time a mid morning influent sample may represent peak loading while the effluent sample represents what entered the plant at minimum load period.

D Changes are the principal reason for sampling and testing for evaluation of treatment performance.

1 Loading may be expected to change by the hour, day, season and population activity both in characteristics and concentration. The long term trend is upward.

2 Water use and requirements change.

3 Physical facilities tend to change with time and use.

4 Operating personnel, capabilities, numbers and motivation change with budgets, organization and public interest.

E Sampling and testing are used to:

1 Estimate work done or remaining to be done.

2 Identify problems.

3 Evaluate problems and response for planning, process techniques or equipment selection, and operational competence purposes.

4 To evaluate compliance with requirements.

F Sampling is the initial step in a complex series such as inspection testing interpretation and active response to information gathered. Many factors affect situation dynamics such as objectives, probabilities, situations, time, money, items to be sampled and particular needs. Manpower capabilities, skills, background, motivation and bias have a large effect upon usefulness of information gathered.

1 There are no fixed rules of sampling applicable to every type of material, item sought situation or purpose.

2 Sampling must be coordinated among those who have or can secure and those who need information. Each must be aware of and respond consistently to site selections, scheduling, techniques and communication to be effective.

3 Integrity and reliability of all personnel concerned are essential. Any lapse in consistency results in loss of control time money with concurrent suspicions with respect to validity of subsequent actions.

G This outline reviews selected factors pertinent to sampling. It is not intended to be complete because situations and needs differ. References (1, 2, 3) cite specifics for each type of item to be analyzed. Each regulatory agency selects certain items from standard compendia that are important to their interest and to those in their jurisdiction. This outline stresses considerations or judgment factors. Authorities specify procedures.

II SAMPLING OBJECTIVES:

Samples are obtained because someone needs precise information about some material, situation or action. Constraints and requirements for sampling and testing depends upon who needs information, what kind, and why. Cost commonly modifies the action.

A Routine Record Sampling Reports:

The major wastewater treatment plant sampling effort commonly is associated with periodic reports to supervisors or regulatory agencies. Sites, frequency, techniques and handling usually are prescribed specifically for the situation by management and/or consultants according to requirements of the regulatory agency. Requirements vary depending upon:

1 Discharge or receiving water quality requirements.

2 Size of the facility.

3 Discharge location in relation to critical reuse of the receiving water.

4 Manpower budget and complexity of treatment.

5 Load characteristics, variation, and their relationships to design loading.

6 Public interest and activity

7 Enforcement

B Process Control Sampling:

Control sampling is intended to estimate what is likely to happen in plant performance rather than what has happened as in routine operating reports. Both record and control sampling and testing are used for performance control. The emphasis for control sampling and testing is to recover information in time for corrective action before little problems become big problems.

1 Control sampling usually is used to characterize in-process variables with respect to stage of completion, environmental condition or rate of change.

2 Control sampling and testing are used to provide rapid estimates of process variables that are relateable to treatment performance and to suggest corrective action when atypical values are evident. Useability is more important than high precision and accuracy.

3 Control information includes sensory impressions, meter readings, biological, chemical or physical criteria. The sampler is expected to note any unusual conditions that may be useful for interpretation of results.

4 Control applications, nature, extent of sampling and testing vary with the treatment and requirements and with staff personnel customs, capabilities, background, motivation and working budget.

C Sampling for Enforcement Purposes:

Much more attention to detail is required for legally acceptable sampling for courtroom procedures than for most other sampling operations.

1 Professionally and legally accepted methods by recognized capable trained personnel are mandatory.

2 Documentation is essential for the history of the sampling operation and subsequent handling. A signed record of time, place, conditions and sample identification number must be logged. The sample requires sealing and tagging for identification and record of who did what and when. Storage and transfer history by responsible individuals is essential.

3 Precise identification procedures, and protection from tampering are main sampling considerations. Any fact of sample history is subject to recall by the court.

4 Careful review of procedures and legal guidance with respect to specifics of the given jurisdiction are important to enhance possibilities for information acceptance by the court.

D Complaint Follow-up:

This usually mea [illegible] special purpose inspection and possible sampling to evaluate the complainant's claim(s) and to guide subsequent action. The complaint may refer to routine or nonroutine characteristics in the collection system treatment plant or receiving water. Prompt and knowledgeable handling in an honest and diplomatic manner including feedback of communication to the complainant through channels are good public relations.

E Treatment Plant Design Data

Much of the information essential for design purposes is available from previous records. Sampling and testing to check routine data and to evaluate unusual or difficulty treatable wastewater mixtures are essential to provide a versatile and reliable facility capable of meeting foreseeable treatment requirements.

1 Loading amount and characteristics including anticipated new contributions and their effects are pertinent.

2 Selection of new processes or new equipment and their performance under conditions similar to that anticipated commonly require sampling and testing.

3 Sampling and testing to meet upgraded performance requirements with supplementary or alternate treatment are indicated.

F Research and Development:

Investigation of new schemes, recombinations of established operations, upgrading treatment with respect to conventional removals or the removal new or different contaminants require a more comprehensive sampling and testing effort than any subsequent application of the same nature. Establishment of guidelines for methodology and interpretation are essential for the different situation.

1 Sampling techniques and frequency for that situation may be different depending on feed or process variability.

2 New interferences may be encountered that require different handling techniques in sampling or testing.

3 Sampling and testing are intended to minimize surprises that may reduce cost effectiveness during subsequent applications.

III SAMPLING PRECAUTIONS BASED UPON ITEMS TO BE SAMPLED

Biological, chemical or physical criteria have their own characteristics and tendencies to change. The sampler should apply suitable techniques to obtain a representative portion of the intended material and to minimize changes before the assay.

A Rapidly reacting chemicals may hydrolyze, oxidize, form addition substitution or complexed products different from those existing at the time of sampling. High rates of component reaction in the sample always complicates sampling precautions and may require the sampler to become an analyst.

1 Storage at low temeratures is common practice for decreasing sample reaction rates. Freezing may be advisable.

2 Biological changes may be reduced by adjusting the sample pH to unfavorably high or low values, or by addition of toxic chemicals.

3 Sample component hydrolysis such as formation of free fatty acids and ammonia from more complex materials is difficult to control. Low temperatures reduce the rate but added preservatives may increase hydrolysis. Prompt determination of unmodified fresh sample material is the best choice in these situations.

4 Chemical addition to convert the item sought into a less reactive derivative may be used effectively such as using zinc salts to enhance possibilities for recovery of sample hydrogen sulfide.

5 Any modification of sample components by addition or other treatment must not interfere with subsequent determinations or alter the quantities of the items sought. The sampler is obligated to use accepted sample modifications only and to clearly identify treatment provided for guidance in testing and interpretation.

B Gas - liquid sampling presents troublesome situations because gas solubility varies with pressure. If the gas is highly reactive such as chlorine, HCN, CO_2, H_2S, O , or NH_3 the problems are magnified.

1 Sampling profiles from top to bottom in tanks means that each 2 feet of depth is associated with a pressure increase of about 1 p.s.i. Gases such as carbon dioxide are much more soluble with increasing depth; CO_2 also tends to be produced in active solids suspensions or deposits. The pH in treatment plant systems changes rapidly with CO_2, HCO_3^- and $CO_3^=$ dynamics. Any pressure reduction or turbulence at reduced pressure enhances loss of CO_2 and concurrent rise in pH of the displaced sample. Electronic sensors and in place measurement of pH permits rapid readout without pressure change effects upon results.

2 Dissolved oxygen solubility varies with temperature and pressure. It also tends to be rapidly used in active systems and may be depleted in deposit vicinities. An oxygen deficient sample rapidly increases in oxygen content upon contact with air. In-place measurement by electronic sensors avoids possible changes due to pressure and reaction.

3 Sampling controls including pressure, chemical fixation, protection from exposure etc., are possible. Chemical fixation such as acid treatment to retain ammonia as ammonium hydrogen sulfate, alkali treatment to retain HCN as sodium cyanide and others have a long history of common use. Elaborate apparatus are available for DO sampling to flush the sample bottle and to minimize subsequent exposure to the air. The apparatus tends to become too elaborate for common use if pressure control is built in.

4 The sampler has become accustomed to measurement of temperature in place and now because he knows that it will change. The treatment plant sampler will perform more effectively if he learns to use additional remote sensors where possible particularly where dissolved gases are concerned.

C Sampling Suspended Materials:

The sampler faces real problems in sampling water containing a conglomerate of operationally defined suspended solids. He is expected to manage representative sampling of a non-homogenous mixture containing items such as organisms, detritus, fibers, grease and chunks of inorganic or organic residues with a wide range of sizes, densities, shapes, and behavior.

1 To be considered as suspended (particulate) material, the mixture must be dispersed in water and tend to move with it. Dissolved materials and rocks are excluded but the suspended material invariably includes dissolved materials, greases, oils, organisms etc. that are mechanically entrapped, adsurbed or otherwise associated with the solids. Suspended solids usually have an additional arbitrary limitation based upon size or ease of separation from water. For example, it is called "grit" if it separates from water suspension within about one minute at a flow velocity of about 1 ft/sec. Chunks, chips and sticks are intended to be removed from the sample.

2 Mixing of the main body of material or flow is essential to disperse components adequately for representative sampling. This requires particular care for raw wastewaters because many contained items tend to slide along the bottom or float at usual flow velocities. Mixing may be performed by a pump, drop box, baffling or other mixing device and the sample site located accordingly.

3 Clearing and cleanup of manual or automatic sample lines and devices are essential. Flushing the lines to obtain free flow before sampling is particularly important for sludge lines because of grease, fibers, sticks etc. in the flow that may partially plug lines.

4 Frequency of sampling depends upon variability if the item tested, requirements of the needed information, money and means to do it. Sludge characteristics may be so variable that it is advisable to sample at 5 minute intervals and composite the series to effectively estimate material pumped.

5 Clarified or stabilized wastewaters are easier to sample because the particulates remaining tend to be more uniformly dispersed. The stabilized wastewaters are easier to sample because the particulates remaining tend to be more uniformly dispersed. The stabilized sample has been equalized and treated in process to decrease the rate of change.

6 Solids have a tendency to change. Dissolved solids may be converted to suspended solids by growth, complexation, sorption or precipitation. Fine particulates tend to become larger particulates by coagulation and agglomeration. Conversely large particulates may be dissolved or dispersed by mixing hydrolysis etc. Cold storage is the usual means of decreasing change rate on samples for solids classification and quantitation. Settling rates should be tested promptly on fresh samples.

D Sampling for Pathogen Determinations

Health hazards related to the likely presence of disease producing organisms in wastewater are a major concern. The sampler is concerned with specific routines characteristic of the particular test organism group, water mass to be sampled and use to be made of the acquired information.

1 Clean sampling containers are required in all sampling routines; in this case, they must also be sterile. Special precautions are required to protect the sample from introduction of extraneous organisms introduced during the sampling operation or subsequent handling.

2 Samples may be stored or transported to the test site under low temperature conditions. No other treatment affecting growth or death rate of the sample organisms is permitted.

3 Time lapse between sampling and determination is critical. Best results are obtained for holding times of less than six hours.

E Other Aquatic Organism Sampling:

Relationships of families of organisms and habitats lead to inferences about conditions depending upon the number and variety of significant organisms in the system. The sampler may be concerned with identification, relative numbers, varieties, predominant groups, selectivity, nutritional status, net growth, environmental conditions, or activities of a biological, chemical or physical nature. Usually treatment plant objectives limit concern to environmental conditions, growth rates, selectivity or activities that are pertinent to treatment plant conditions and can be observed or measured effectively.

1 Biomonitoring, oxygen use rates, growth rates and dynamics of organism or substrate selection necessarily require fresh samples under favorable environmental conditions.

2 Net changes, accumulated cell mass and residue accumulation may be preserved and tested later.

3 Frequent and varied sampling and testing of environmental conditions are essential to permit interpretations of behavior. Toxicity information on a test material lacks validity if later information suggests that oxygen starvation may have been a factor.

4 Direct observation on fresh process samples of selected indicator organisms commonly found under favorable performance conditions are useful. Sudden disappearance or inactivity of the usual critters suggest drastic changes in conditions or process.

IV SUMMARY:

A The sampler is obligated to follow prescribed sampling sites, methodology, scheduling and routing of samples agreed upon for his situation.

B Sampling integrity is essential. The sample should be clearly identified and represent the material to be sampled at the time and place designated. Any unusual conditions on site that may affect results should be noted in the sample record. The sample should be protected from tampering. Preservatives, storage conditions, and routine or special handling should be as specified and part of the record.

C Sampling information in this outline is deliberately selective and incomplete for guidance considerations. References cited include much more detail concerning sampling and sample handling depending on sampled material, determinations to be made, and use of the information. It must be noted that any "Standard" methods compendium includes professionally recognized and recommended procedures including certain alternates and options. These do not become legally recognized methods until accepted by statute or by the designated statutory authorities, rules and regulations for their jurisdiction. It is necessary to determine which of the possible options are acceptable within a given jurisdiction.

REFERENCES:

1 Standard Methods. Water and Wastewater 13th Edition 1971 APHA, AWWA, WPCF.

2 1971 Annual Book of ASTM Standards, Part 23 Water: Atmospheric Analysis. American Society for Testing and Materials.

3 Methods for Chemical Analysis of Water and Wastes 1971. USEPA, Office of Water Quality, Analytical Quality Control Laboratory.

4 Rules and Regulations of the Water Quality Enforcement Agency(s) including your area of operations.

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DISSOLVED OXYGEN DETERMINATION (DO) - I

Winkler Iodometric Titration and Azide Modification

I The Dissolved Oxygen determination is a very important water quality criteria for many reasons:

A Oxygen is an essential nutrient for all living organisms. Dissolved oxygen is essential for survival of aerobic organisms and permits facultative organisms to metabolize more effectively. Many desirable varieties of macro or micro organisms cannot survive at dissolved oxygen concentrations below certain minimum values. These values vary with the type of organisms, stage in their life history, activity, and other factors.

B Dissolved oxygen levels may be used as an indicator of pollution by oxygen demanding wastes. Low DO concentrations are likely to be associated with low quality waters.

C The presence of dissolved oxygen prevents or minimizes the onset of putrefactive decomposition and the production of objectionable amounts of malodorous sulfides, mercaptans, amines, etc.

D Dissolved oxygen is essential for terminal stabilization wastewaters. High DO concentrations are normally associated with good quality water.

E Dissolved oxygen changes with respect to time, depth or section of a water mass are useful to indicate the degree of stability or mixing characteristics of that situation.

F The BOD or other respirometric test methods for water quality are commonly based upon the difference among an initial and final DO determination for a given sample time interval and condition. These measurements are useful to indicate:

1 The rate of biochemical activity in terms of oxygen demand for a given sample and conditions.

2 The degree of acceptability (a bioassay technique) for biochemical stabilization of a given microbiota in response to food, inhibitory agents or test conditions.

3 The degree of instability of a water mass on the basis of test sample DO changes over an extended interval of time.

4 Permissible load variations in surface water or treatment units in terms of DO depletion versus time, concentration, or ratio of food to organism mass, solids, or volume ratios.

5 Oxygenation requirements necessary to meet the oxygen demand in treatment units or surface water situations.

G The DO test is the only chemical test included in all Water Quality Criteria, Federal, State, Regional or local.

II FACTORS AFFECTING THE DO CONCENTRATION IN WATER

A Physical Factors:

1 DO solubility in water for an air/water system is limited to about 9 mg DO/liter of water at 20° C. This amounts to about 0.0009% as compared to 21% by weight of oxygen in air.

2 Transfer of oxygen from air to water is limited by the interface area, the oxygen deficit, partial pressure, the conditions at the

interface area, mixing phenomena and other items.

Certain factors tend to confuse reoxygenation mechanisms of water aeration:

a The transfer of oxygen in air to dissolved molecular oxygen in water has two principal variables:

1) Area of the air-water interface.

2) Dispersion of the oxygen-saturated water at the interface into the body liquid.

The first depends upon the surface area of the air bubbles in the water or water drops in the air; the second depends upon the mixing energy in the liquid. If diffusors are placed in a line along the wall, dead spots may develop in the core. Different diffusor placement or mixing energy may improve oxygen transfer to the liquid two or threefold.

b Other variables in oxygen transfer include:

3) Oxygen deficit in the liquid.

4) Oxygen content of the gas phase.

5) Time.

If the first four variables are favorable, the process of water oxygenation is rapid until the liquid approaches saturation. Much more energy and time are required to increase oxygen saturation from about 95 to 100% than to increase oxygen saturation from 0 to about 95%. For example: An oxygen-depleted sample often will pick up significant DO during DO testing; changes are unlikely with a sample containing equilibrium amounts of DO.

c The limited solubility of oxygen in water compared to the oxygen content of air does not require the interchange of a large mass of oxygen per unit volume of water to change DO saturation. DO increases from zero to 50% saturation are common in passage over a weir.

d Aeration of dirty water is practiced for cleanup. Aeration of clean water results in washing the air and transferring fine particulates and gaseous contaminants to the liquid.

e One liter of air at room temperature contains about 230 mg of oxygen. A 5 gal carboy of water with 2 liters of gas space above the liquid has ample oxygen supply for equilibration of DO after storage for 2 or 3 days or shaking for 30 sec.

f Aeration tends toward evaporative cooling. Oxygen content becomes higher than saturation values at the test temperature, thus contributing to high blanks.

3 Oxygen solubility varies with the temperature of the water. Solubility at 10° C is about two times that at 30° C. Temperature often contributes to DO variations much greater than anticipated by

solubility. A cold water often has much more DO than the solubility limits at laboratory temperature. Standing during warmup commonly results in a loss of DO due to oxygen diffusion from the supersaturated sample. Samples warmer than laboratory temperature may decrease in volume due to the contraction of liquid as temperature is lowered. The full bottle at higher temperature will be partially full after shrinkage with air entrance around the stopper to replace the void. Oxygen in the air may be transferred to raise the sample DO. For example, a volumetric flask filled to the 1000 ml mark at 30° C will show a water level about 1/2 inch below the mark when the water temperature is reduced to 20° C. BOD dilutions should be adjusted to 20° C + or - 1 1/2° before filling and testing.

4 Water density varies with temperature with maximum water density at 4° C. Colder or warmer waters tend to promote stratification of water that interferes with distribution of DO because the higher density waters tend to seek the lower levels.

5 Oxygen diffusion in a water mass is relatively slow, hence vertical and lateral mixing are essential to maintain relatively uniform oxygen concentrations in a water mass.

6 Increasing salt concentration decreases oxygen solubility slightly but has a larger effect upon density stratification in a water mass.

7 The partial pressure of the oxygen in the gas above the water interface controls the oxygen solubility limits in the water. For example, the equilibrium concentration of oxygen in water is about 9 mg DO/l under one atmospheric pressure of air, about 42 mg DO/liter in contact with pure oxygen and 0 mg DO/liter in contact with pure nitrogen (@ 20° C).

B Biological or Bio-Chemical Factors

1 Aquatic life requires oxygen for respiration to meet energy requirements for growth, reproduction, and motion. The net effect is to deplete oxygen resources in the water at a rate controlled by the type, activity, and mass of living materials present, the availability of food and favorability of conditions.

2 Algae, autotrophic bacteria, plants or other organisms capable of photosynthesis may use light energy to synthesize cell materials from mineralized nutrients with oxygen released in process.

a Photosynthesis occurs only under the influence of adequate light intensity.

b Respiration of alga is continuous.

c The dominant effect in terms of oxygen assets or liabilities of alga depends upon algal activity, numbers and light intensity. Gross algal productivity contributes to significant diurnal DO variations.

3 High rate deoxygenation commonly accompanies assimilation of readily available nutrients and conversion into cell mass or storage products. Deoxygenation due to cell mass respiration commonly occurs at some lower rate dependent upon the nature of the organisms present, the stage of decomposition and the degree of predation, lysis, mixing and regrowth. Relatively high

deoxygenation rates commonly are associated with significant growth or regrowth of organisms.

4 Micro-organisms tend to flocculate or agglomerate to form settleable masses particularly at limiting nutrient levels (after available nutrients have been assimilated or the number of organisms are large in proportion to available food).

a Resulting benthic deposits continue to respire as bed loads.

b Oxygen availability is limited because the deposit is physically removed from the source of surface oxygenation and algal activity usually is more favorable near the surface. Stratification is likely to limit oxygen transfer tothe bed load vicinity.

c The bed load commonly is oxygen deficient and decomposes by anaerobic action.

d Anaerobic action commonly is characterized by a dominant hydrolytic or solubilizing action with relatively low rate growth of organisms.

e The net effect is to produce low molecular weight products from cell mass with a correspondingly large fraction of feedback of nutrients to the overlaying waters. These lysis products have the effect of a high rate or immediate oxygen demand upon mixture with oxygen containing waters.

f Turbulence favoring mixing of surface waters and benthic sediments commonly are associated with extremely rapid depletion of DO. Recurrent resuspension of thin benthic deposits may contribute to highly erratic DO patterns.

g Long term deposition areas commonly act like point sources of new pollution as a result of the feedback of nutrients from the deposit. Rate of reaction may be low for old materials but a low percentage of a large mass of unstable material may produce excessive oxygen demands.

C Tremendous DO variations are likely in a polluted water in reference to depth, cross section or time of day. More stabilized waters tend to show decreased DO variations although it is likely that natural deposits such as leaf mold will produce differences related to depth in stratified deep waters.

III ANALYTICAL METHOD BACKGROUND

The basic Winkler procedure (1888) has been modified many times to improve its workability in polluted waters. None of these modifications have been completely successful. The most useful modification was proposed by Alsterberg and consists of the addition of sodium azide to control nitrite interference during the iodometric titration. The Azide modification of the iodometric titration is recommended as official by the EPA-OWP Quality Control Committee for relatively clean waters.

A Reactions

1 The determination of DO involves a complex series of interactions that must be quantitative to provide a valid DO result. The number of sequential reactions also complicates interference control. The reactions will be presented first followed by discussion of the functional aspects.

$MnSO_4 + 2\ KOH \rightarrow Mn(OH)_2 + K_2SO_4$ (a)

$2\ Mn(OH)_2 + O_2 \rightarrow 2\ MnO(OH)_2$ (b)

$MnO(OH)_2 + 2\ H_2SO_4 \rightarrow Mn(SO_4)_2 + 3H_2O$ (c)

$Mn(SO_4)_2 + 2\ KI \rightarrow MnSO_4 + K_2SO_4 + I_2$ (d)

$I_2 + 2\ Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2\ NaI$ (e)

2 Reaction sequence

The series of reactions involves five different operational steps in converting dissolved oxygen in the water into a form in which it can be measured.

a $O_2 \rightarrow MnO(OH)_2 \rightarrow Mn(SO_4)_2 \rightarrow I_2 \rightarrow$ Thiosulfate (thio) or phenylarsine oxide (PAO) titration.

b All added reagents are in excess to improve contact possibilities and to force the reaction toward completion.

3 The first conversion, $O_2 \rightarrow MnO(OH)_2$ (reactions a, b) is an oxygen transfer operation where the dissolved oxygen in the water combines with manganous hydroxide to form an oxygenated manganic hydroxide.

a The manganous salt can react with oxygen only in a highly alkaline media.

b The manganous salt and alkali must be added separately with addition below the surface of the sample to minimize reaction with atmospheric oxygen via air bubbles or surface contact. Reaction with sample dissolved oxygen is intended to occur upon mixing of the reagents and sample after stoppering the full bottle (care should be used to allow entrained air bubbles to rise to the surface before adding reagents to prevent high results due to including entrained oxygen).

c Transfer of oxygen from the dissolved state to the precipitate form involves a two phase system of solution and precipitate requiring effective mixing for quantitative transfer. Normally a gross excess of reagents are used to limit mixing requirements. Mixing by rapid inversion 25 to 35 times will accomplish the purpose. Less energy is required by inversion 5 or 6 times, allowing the solids to settle half way and repeat the process. Reaction is rapid; contact is the principal problem in the two phase system.

d If the alkaline floc is white, no oxygen is present.

4 Acidification (reactions c and d) changes the oxygenated manganic hydroxide to manganic sulfate which in turn reacts with potassium iodide to form elemental iodine. Under acid conditions, oxygen cannot react directly with the excess manganous sulfate remaining in solution.

5 Iodine (reaction e) may be titrated with sodium thiosulfate standard solution to indicate the amount of dissolved oxygen originally present in the sample.

a The blue color of the starch-iodine complex commonly is used as an indicator. This blue color disappears when elemental iodine has been reacted with an equivalent amount of thiosulfate.

b Phenylarsine oxide solutions are more expensive to obtain but have better keeping qualities than thiosulfate solutions. Occasional use, field operations and situations where it is not feasible to calibrate thio solutions regularly, usually encourage use of purchased PAO reagents.

6 For practical purposes the DO determination scheme involves the following operations.

a Fill a 300 ml bottle* under conditions minimizing DO changes. This means that the sample bottle must be flushed with test solution to displace the air in the bottle with water characteristic of the tested sample*.

*DO test bottle volumes should be checked - discard those outside of the limits of 300 ml + or - 3 ml.

b To the filled bottle:

1) Add $MnSO_4$ reagent (2 ml)

2) Add KOH, KI, NaN_3 reagent (2 ml)
Stopper, mix by inversion, allow to settle half way and repeat the operation. Highly saline test waters commonly settle very slowly at this stage and may not settle to the half way point in the time allotted.

c To the alkaline mix (settled about half way) add 2 ml of sulfuric acid, stopper and mix until the precipitate dissolves.

d Transfer the contents of the bottle to a 500 ml Erlenmeyer flask and titrate with 0.0375 Normal Thiosulfate*. Each ml of reagent used represents 1 mg of DO/liter of sample.

The same thing applies for other sample volumes when using an appropriate titrant normality such as:

1) For a 200 ml sample, use 0.025 N Thio

2) For a 100 ml sample, use 0.0125 N Thio

*EPA-WPO Method

7 The addition of the first two DO reagents, ($MnSO_4$ and the KOH, KI and NaN_3 solutions) displaces an equal quantity of the sample. This is not the case when acid is added because the clear liquid above the floc does not contain dissolved oxygen as all of it should be converted to the particulate $MnO(OH)_2$. Some error is introduced by this displacement of sample during dosage of the first two reagents. The error upon addition of 2 ml of each reagent to a 300 ml sample is $\frac{4}{300} \times 100$ or 1.33% loss in DO. This may be corrected by an appropriate factor or by adjustment of reagent normality. It is generally considered small in relation to other errors in sampling, manipulation and interference, hence this error may be recognized but not corrected.

8 Reagent preparation and procedural details can be found in reference 1.

IV The sequential reactions for the Chemical DO determination provides several situations where significant interference may occur in application on polluted water, such as:

A Sampling errors may not be strictly designated as interference but have the same effect of changing sample DO. Inadequate flushing of the bottle contents or exposure to air may raise the DO of low oxygen samples or lower the DO of supersaturated samples.

B Entrained air may be trapped in a DO bottle by:

1 Rapid filling of vigorously mixed samples without allowing the entrained air to escape before closing the bottle and adding DO reagents.

2 Filling a bottle with low temperature water holding more DO than that in equilibrium after the samples warm to working temperature.

3 Aeration is likely to cool the sample permitting more DO to be introduced than can be held at the room or incubator temperatures.

4 Samples warmer than working incubator temperatures will be only partially full at equilibrium temperatures.

Addition of DO reagents results in reaction with dissolved or entrained oxygen. Results for DO are invalid if there is any evidence of gas bubbles in the sample bottle.

C The DO reagents respond to any oxidant or reductant in the sample capable of reacting within the time allotted. HOCl of H_2O_2 may raise the DO titration while H_2S, 4 SH^- may react with sample oxygen to lower the sample titration. The items mentioned react rapidly and raise or lower the DO result promptly. Other items such as Fe^{++} or $SO_3^{=}$ may or may not react completely within the time allotted for reaction. Many organic materials or complexes from benthic deposits may have an effect upon DO results that are difficult to predict. They may have one effect during the alkaline stage to release iodine from KI while favoring irreversible absorption of iodine during the acid stage. Degree of effect may increase with reaction time. It is generally inadvisable to use the iodometric titration on samples containing large amounts of organic contaminants or benthic residues. It would be expected that benthic residues would tend toward low results because of the reduced iron and sulfur content - they commonly favor high results due to other factors that react more rapidly, often giving the same effect as in uncontrolled nitrite interference during titration.

D Nitrite is present to some extent in natural waters or partially oxidized treatment plant samples. Nitrite is associated with a cyclic reaction during the acid stage of the DO determination that may lead to erroneous high results.

1 These reactions may be represented as follows:

$$
\begin{array}{lr}
2HNO_2 + 2\,HI \rightarrow I_2 + 4H_2O + N_2O_2 & (a) \\
\uparrow \qquad\qquad\qquad\qquad\qquad\qquad\quad \downarrow & \\
2HNO_2 \leftarrow + 1/2O_2 + H_2O + N_2O_2 & (b)
\end{array}
$$

These reactions are time, mixing and concentration dependent and can be minimized by rapid processing.

2 Sodium azide (NaN_3) reacts with nitrite under acid conditions to form a combination of $N_2 + N_2O$ which effectively blocks the cyclic reaction by converting the HNO_2 to noninterfering compounds of nitrogen.

3 Sodium azide added to fresh alkaline KI reagent is adequate to control interference up to about 20 mg of HNO_2 - N/liter of sample. The azide is unstable and gradually decomposes. If resuspended benthic sediments are not detectable in a sample showing a returning blue color, it is likely that the azide has decomposed in the alkaline KI azide reagent.

E Surfactants, color and Fe+++ may confuse endpoint detection if present in significant quantities.

F Polluted water commonly contains significant interferences such as C. It is advisable to use a membrane protected sensor of the electronic type for DO determinations in the presence of these types of interference.

G The order of reagent addition and prompt completion of the DO determination is critical. Stable waters may give valid DO results after extended delay of titration during the acidified stage. For unstable water, undue delay at any stage of processing accentuates interference problems.

ACKNOWLEDGMENTS

This outline contains significant materials from previous outlines by J. W. Mandia. Review and comments by C. R. Hirth and R. L. Booth are greatly appreciated.

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This outline was prepared by F. J. Ludzack, Chemist, National Training Center, MDS, WPQ EPA, Cincinnati, OH 45268.

DISSOLVED OXYGEN DETERMINATION - II
ELECTRONIC MEASUREMENTS

I INTRODUCTION

A Electronic measurement of DO is attractive for several reasons:

1 Electronic methods are more readily adaptable for automated analysis, continuous recording, remote sensing or portability.

2 Application of electronic methods with membrane protection of sensors affords a high degree of interference control.

3 Versatility of the electronic system permits design for a particular measurement, situation or use.

4 Many more determinations per manhour are possible with a minor expenditure of time for calibration.

B Electronic methods of analysis impose certain restrictions upon the analyst to insure that the response does, in fact, indicate the item sought.

1 The ease of reading the indicator tends to produce a false sense of security. Frequent and careful calibrations are essential to establish workability of the apparatus and validity of its response.

2 The use of electronic devices requires a greater degree of competence on the part of the analyst. Understanding of the behavior of oxygen must be supplemented by an understanding of the particular instrument and its behavior during use.

C Definitions

1 Electrochemistry - a branch of chemistry dealing with relationships between electrical and chemical changes.

2 Electronic measurements or electrometric procedures - procedures using the measurement of potential differences as an indicator of reactions taking place at an electrode or plate.

3 Reduction - any process in which one or more electrons are added to an atom or an ion, such as $O_2 + 2e \rightarrow 20^{-}$! The oxygen has been reduced.

4 Oxidation - any process in which one or more electrons are removed from an atom or an ion, such as $Zn^{o} - 2e \rightarrow Zn^{+2}$. The zinc has been oxidized.

5 Oxidation - reduction reactions - in a strictly chemical reaction, reduction cannot occur unless an equivalent amount of some oxidizable substance has been oxidized. For example:

$2H_2 + O_2 \rightleftarrows 2H_2O$

$2H_2 - 4e \rightleftarrows 4H^{+1}$ hydrogen oxidized

$O_2 + 4e \rightleftarrows 20^{-2}$ oxygen reduced

Chemical reduction of oxygen may also be accomplished by electrons supplied to a noble metal electrode by a battery or other energizer.

6 Anode - an electrode at which oxidation of some reactable substance occurs.

7 Cathode - an electrode at which reduction of some reactable substance occurs. For example in I. C. 3, the reduction of oxygen occurs at the cathode.

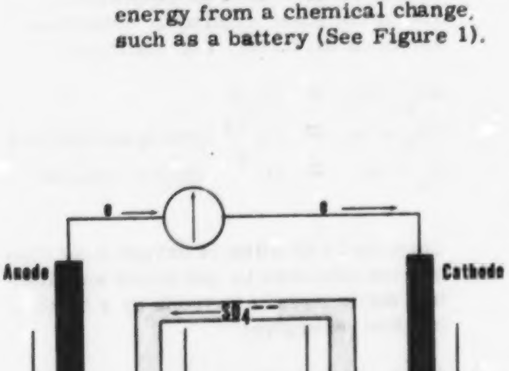
8 Electrochemical reaction - a reaction involving simultaneous conversion of chemical energy into electrical energy or the reverse. These conversions are

equivalent in terms of chemical and electrical energy and generally are reversible.

9 Electrolyte a solution, gel, or mixture capable of conducting electrical energy and serving as a reacting media for chemical changes. The electrolyte commonly contains an appropriate concentration of selected mobile ions to promote the desired reactions.

10 Electrochemical cell - a device consisting of an electrolyte in which 2 electrodes are immersed and connected via an external metallic conductor. The electrodes may be in separate compartments connected by tube containing electrolyte to complete the internal circuit.

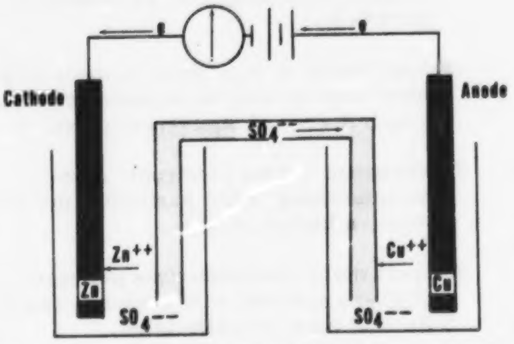
a Galvanic (or voltaic) cell - an electrochemical cell operated in such a way as to produce electrical energy from a chemical change, such as a battery (See Figure 1).



GALVANIC CELL

Figure 1

b Polarographic (electrolytic) cell - an electrochemical cell operated in such a way as to produce a chemical change from electrical energy (See Figure 2).



POLAROGRAPHIC CELL

Figure 2

D As indicated in I. C. 10 the sign of an electrode may change as a result of the operating mode. The conversion by the reactant of primary interest at a given electrode therefore designates terminology for that electrode and operating mode. In electronic oxygen analyzers, the electrode at which oxygen reduction occurs is designated the cathode.

E Each cell type has characteristic advantages and limitations. Both may be used effectively.

1 The galvanic cell depends upon measurement of electrical energy produced as a result of oxygen

reduction. If the oxygen content of the sample is negligible, the measured current is very low and indicator driving force is negligible, therefore response time is longer.

2 The polarographic cell uses a standing current to provide energy for oxygen reduction. The indicator response depends upon a change in the standing current as a result of electrons released during oxygen reduction. Indicator response time therefore is not dependent upon oxygen concentration.

3 Choice may depend upon availability, habit, accessories, or the situation. In each case it is necessary to use care and judgment both in selection and use for the objectives desired.

II ELECTRONIC MEASUREMENT OF DO

A Reduction of oxygen takes place in two steps as shown in the following equations:

1 $O_2 + 2H_2O + 2e \rightarrow H_2O_2 + 2OH^-$

2 $H_2O_2 + 2e^- \rightarrow 2OH^-$

Both equations require electron input to activate reduction of oxygen. The first reaction is more important for electronic DO measurement because it occurs at a potential (voltage) which is below that required to activate reduction of most interfering components (0.3 to 0.8 volts relative to the saturated calomel electrode - SCE). Interferences that may be reduced at or below that required for oxygen usually are present at lower concentrations in water or may be minimized by the use of a selective membrane or other means. When reduction occurs, a definite quantity of electrical energy is produced that is proportional to the quantity of reductant entering the reaction. Resulting current measurements thus are more specific for oxygen reduction.

B Most electronic measurements of oxygen are based upon one of two techniques for evaluating oxygen reduction in line with equation II.A.1. Both require activating energy, both produce a current proportional to the quantity of reacting reductant. The techniques differ in the means of supplying the activating potential; one employs a source of outside energy, the other uses spontaneous energy produced by the electrode pair.

1 The polarographic oxygen sensor relies upon an outside source of potential to activate oxygen reduction. Electron gain by oxygen changes the reference voltage.

a Traditionally, the dropping mercury electrode (DME) has been used for polarographic measurements. Good results have been obtained for DO using the DME but the difficulty of maintaining a constant mercury drop rate, temperature control, and freedom from turbulence makes it impractical for field use.

b Solid electrodes are attractive because greater surface area improves sensitivity. Poisoning of the solid surface electrodes is a recurrent problem. The use of selective membranes over noble metal electrodes has minimized but not eliminated electrode contamination. Feasibility has been improved sufficiently to make this type popular for regular use.

2 Galvanic oxygen electrodes consist of a decomposable anode and a noble metal cathode in a suitable electrolyte to produce activating energy for oxygen reduction (an air cell or battery). Lead is commonly used as the anode because its decomposition potential favors spontaneous reduction of oxygen. The process is continuous as long as lead and oxygen are in contact in the electrolyte and the electrical energy released at the cathode may be dissipated by an outside circuit. The anode may be conserved by limiting oxygen availability. Interrupting the outside circuit may produce erratic behavior for a time after reconnection. The resulting

current produced by oxygen reduction may be converted to oxygen concentration by use of a sensitivity coefficient obtained during calibration. Provision of a pulsed or interrupted signal makes it possible to amplify or control the signal and adjust it for direct reading in terms of oxygen concentration or to compensate for temperature effects.

III ELECTRONIC DO ANALYZER APPLICATION FACTORS

A Polarographic or galvanic DO instruments operate as a result of oxygen partial pressure at the sensor surface to produce a signal characteristic of oxygen reduced at the cathode of some electrode pair. This signal is conveyed to an indicating device with or without modification for sensitivity and temperature or other influences depending upon the instrument capabilities and intended use.

1 Many approaches and refinements have been used to improve workability, applicability, validity, stability and control of variables. Developments are continuing. It is possible to produce a device capable of meeting any reasonable situation, but situations differ.

2 Most commercial DO instruments are designed for use under specified conditions. Some are more versatile than others. Benefits are commonly reflected in the price. It is essential to determine the requirements of the measurement situation and objectives for use. Evaluation of a given instrument in terms of sensitivity, response time, portability, stability, service characteristics, degree of automation, and consistency are used for judgment on a cost/benefit basis to select the most acceptable unit.

B Variables Affecting Electronic DO Measurement

1 Temperature affects the solubility of oxygen, the magnitude of the resulting signal and the permeability of the protective membrane. A curve of oxygen solubility in water versus increasing temperature may be concave downward while a similar curve of sensor response versus temperature is concave upward. Increasing temperature decreases oxygen solubility and increases probe sensitivity and membrane permeability. Thermistor actuated compensation of probe response based upon a linear relationship or average of oxygen solubility and electrode sensitivity is not precisely correct as the maximum spread in curvature occurs at about 17° C with lower deviations from linearity above or below that temperature. If the instrument is calibrated at a temperature within + or - 5° C of working temperature, the compensated readout is likely to be within 2% of the real value. Depending upon probe geometry, the laboratory sensor may require 4 to 6% correction of signal per ° C change in liquid temperature.

2 Increasing pressure tends to increase electrode response by compression and contact effects upon the electrolyte, dissolved gases and electrode surfaces. As long as entrained gases are not contained in the electrolyte or under the membrane, these effects are negligible.

Inclusion of entrained gases results in erratic response that increases with depth of immersion.

3 Electrode sensitivity changes occur as a result of the nature and concentration of contaminants at the electrode surfaces and possible physical chemical or electronic side reactions produced. These may take the form of a physical barrier, internal short, high residual current, or chemical changes in the metal surface. The membrane is intended to allow dissolved gas penetration but to exclude passage of ions or particulates. Apparently some ions or materials producing extraneous ions within the electrode vicinity are able to pass in limited amounts which

become significant in time. Dissolved gases include 1) oxygen, 2) nitrogen, 3) carbon dioxide, 4) hydrogen sulfide, and certain others. Item 4 is likely to be a major problem. Item 3 may produce deposits in alkaline media; most electrolytes are alkaline or tend to become so in line with reaction II.A.1. The usable life of the sensor varies with the type of electrode system, surface area, amount of electrolyte and type, membrane characteristics, nature of the samples to which the system is exposed and the length of exposure. For example, galvanic electrodes used in activated sludge units showed that the time between cleanup was 4 to 6 months for electrodes used for intermittent daily checks of effluent DO; continuous use in the mixed liquor required electrode cleanup in 2 to 4 weeks. Each electrometric cell configuration and operating mode has its own response characteristics. Some are more stable than others. It is necessary to check calibration frequency required under conditions of use as none of them will maintain uniform response indefinitely. Calibration before and after daily use is advisable.

4 Electrolytes may consist of solutions or gels of ionizable materials such as acids, alkalies or salts. Bicarbonates, KC1 and KI are frequently used. The electrolyte is the transfer and reaction media, hence, it necessarily becomes contaminated before damage to the electrode surface may occur. Electrolyte concentration, nature, amount and quality affect response time, sensitivity, stability, and specificity of the sensor system. Generally a small quantity of electrolyte gives a shorter response time and higher sensitivity but also may be affected to a greater extent by a given quantity of contaminating substances.

5 Membranes may consist of teflon, polyethylene, rubber, and certain other polymeric films. Thickness may vary from 0.5 to 3 mils (inches × 1/1000). A thinner membrane will decrease response time and increase sensitivity but is less selective and may be ruptured more easily. The choice of material and its uniformity affects response time, selectivity and durability. The area of the membrane and its permeability are directly related to the quantity of transported materials that may produce a signal. The permeability of the membrane material is related to temperature and to residues accummulated on the membrane surface or interior. A cloudy membrane usually indicates deposition and more or less loss of signal.

6 Test media characteristics control the interval of usable life between cleaning and rejuvenation for any type of electrode. More frequent cleanup is essential in low quality waters than for high quality waters. Reduced sulfur compounds are among the more troublesome contaminants. Salinity affects the partial pressure of oxygen at any given temperature. This effect is small compared to most other variables but is significant if salinity changes by more than 500 mg/l.

7 Agitation of the sample in the vicinity of the electrode is important because DO is reduced at the cathode. Under quiescent conditions a gradient in dissolved oxygen content would be established on the sample side of the membrane as well as on the electrode side, resulting in atypical response. The sample should be agitated sufficiently to deliver a representative portion of the main body of the liquid to the outer face of the membrane. It is commonly observed that no agitation will result in a very low or negigible response after a short period of time. Increasing agitation will cause the response to rise gradually until some minimum liquid velocity is reached that will not cause a further increase in response with increased mixing energy. It is important to check mixing velocity to reach a stable high signal that is independent of a reasonable change in sample mixing. Excessive

mixing may create a vortex and expose the sensing surface to air rather than sample liquid. This should be avoided. A linear liquid velocity of about 1 ft/sec at the sensing surface is usually adequate.

8 DO sensor response represents a potential or current signal in the milli-volt or milli-amp range in a high resistance system. A high quality electronic instrument is essential to maintain a usable signal-to-noise ratio. Some of the more common difficulties include:

  a Variable line voltage or low batteries in amplifier power circuits.

  b Substandard or unsteady amplifier or resistor components.

  c Undependable contacts or junctions in the sensor, connecting cables, or instrument control circuits.

  d Inadequately shielded electronic components.

  e Excessive exposure to moisture, fumes or chemicals in the wrong places lead to stray currents, internal shorts or other malfunction.

C Desirable Features in a Portable DO Analyzer

1 The unit should include steady state performance electronic and indicating components in a convenient but sturdy package that is small enough to carry.

2 There should be provisions for addition of special accessories such as bottle or field sensors, agitators, recorders, line extensions, if needed for specific requirements. Such additions should be readily attachable and detachable and maintain good working characteristics.

3 The instrument should include a sensitivity adjustment which upon calibration will provide for direct reading in terms of mg of DO/liter.

4 Temperature compensation and temperature readout should be incorporated.

5 Plug in contacts should be positive, sturdy, readily cleanable and situated to minimize contamination. Water seals should be provided where necessary.

6 The sensor should be suitably designed for the purpose intended in terms of sensitivity, response, stability, and protection during use. It should be easy to clean, and reassemble for use with a minimum loss of service time.

7 Switches, connecting plugs, and contacts preferably should be located on or in the instrument box rather than at the "wet" end of the line near the sensor. Connecting cables should be multiple strand to minimize separate lines. Calibration controls should be convenient but designed so that it is not likely that they will be inadvertently shifted during use.

8 Agitator accessories for bottle use impose special problems because they should be small, self contained, and readily detachable but sturdy enough to give positive agitation and electrical continuity in a wet zone.

9 Major load batteries should be rechargeable or readily replaceable. Line operation should be feasible wherever possible.

10 Service and replacement parts availability are a primary consideration. Drawings, parts identification and trouble shooting memos should be incorporated with applicable operating instructions in the instrument manual in an informative organized form.

D Sensor and Instrument Calibration

The instrument box is likely to have some form of check to verify electronics, battery or other power supply conditions for use. The sensor commonly is not included in this check. A known reference sample used with the instrument in an operating mode is the best available method to compensate for sensor variables under use conditions. It is advisable to calibrate before and after daily use under test conditions. Severe conditions, changes in conditions, or possible damage call for calibrations during the use period. The readout scale is likely to be labeled - calibration is the basis for this label.

The following procedure is recommended:

1 Turn the instrument on and allow it to reach a stable condition. Perform the recommended instrument check as outlined in the operating manual.

2 The instrument check usually includes an electronic zero correction. Check each instrument against the readout scale with the sensor immersed in an agitated solution of sodium sulfite containing sufficient cobalt chloride to catalyze the reaction of sulfite and oxygen. The indicator should stabilize on the zero reading. If it does not, it may be the result of residual or stray currents, internal shorting in the electrode, or membrane rupture. Minor adjustments may be made using the indicator rather than the electronic controls. Serious imbalance requires electrode reconditioning if the electronic check is O.K. Sulfite must be carefully rinsed from the sensor until the readout stabilizes to prevent carry over to the next sample.

3 Fill two DO bottles with replicate samples of clarified water similar to that to be tested. This water should not contain significant test interferences.

4 Determine the DO in one by the azide modification of the iodometric titration.

5 Insert a magnetic stirrer in the other bottle or use a probe agitator. Start agitation after insertion of the sensor assembly and note the point of stabilization.

a Adjust the instrument calibration control if necessary to compare with the titrated DO.

b If sensitivity adjustment is not possible, note the instrument stabilization point and designate it as ua. A sensitivity coefficient, ϕ is equal to $\frac{ua}{DO}$ where DO is the titrated value for the sample on which ua was obtained. An unknown DO then becomes $DO = \frac{ua}{\phi}$. This factor is applicable as long as the sensitivity does not change.

6 Objectives of the test program and the type of instrument influence calibration requirements. Precise work may require calibration at 3 points in the DO range of interest instead of at zero and high range DO. One calibration point frequently may be adequate.

Calibration of a DO sensor in air is a quick test for possible changes in sensor response. The difference in oxygen content of air and of water is too large for air calibration to be satisfactory for precise calibration for use in water.

IV This section reviews characteristics of several sample laboratory instruments. Mention of a specific instrument does not imply EPA endorsement or recommendation. No attempt has been made to include all the available instruments; those described are used to indicate the approach used at one stage of development which may or may not represent the current available model.

A The electrode described by Carrit and Kanwisher (1) is illustrated in Figure 3. This electrode was an early example of those using a membrane. The anode was a silver - silver oxide reference cell with a platinum disc cathode (1-3 cm diameter). The salt bridge consisted of N/2 KCl and

KOH. The polyethylene membrane was held in place by a retaining ring. An applied current was used in a polarographic mode. Temperature effects were relatively large. Thermistor correction was studied but not integrated with early models.

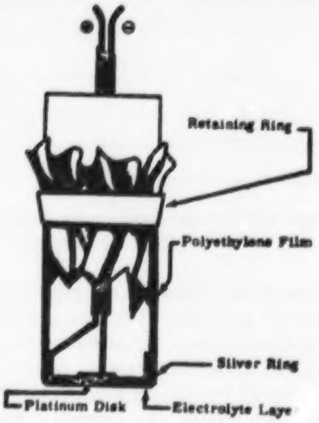

Retaining Ring
Polyethylene Film
Silver Ring
Platinum Disk
Electrolyte Laye

Figure 3

B The Beckman oxygen electrode is another illustration of a polarographic DO sensor (Figure 4). It consists of a gold cathode, a silver anode, an electrolytic gel containing KCl, covered by a teflon membrane. The instrument has a temperature readout and compensating thermistor, a source polarizing current, amplifier with signal adjustment and a readout DO scale with recorder contacts.

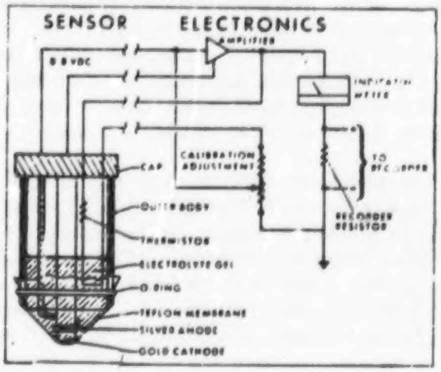

SENSOR
ELECTRONICS
AMPLIFIER
INDICATING METER
CALIBRATION ADJUSTMENT
TO RECORDER
RECORDER RESISTOR
CAP
OUTER BODY
THERMISTOR
ELECTROLYTE GEL
O RING
TEFLON MEMBRANE
SILVER ANODE
GOLD CATHODE

Figure 4. THE BECKMAN OXYGEN SENSOR

C The YSI Model 51 (3) is illustrated in Figure 5. This is another form of polarographic DO analyzer. The cell consists of a silver anode coil, a gold ring cathode and a KCl electrolyte with a teflon membrane. The instrument has a sensitivity adjustment, temperature and DO readout. The model 51 A has temperature compensation via manual preset dial. A field probe and bottle probe are available.

YSI Model 51 DO Sensor

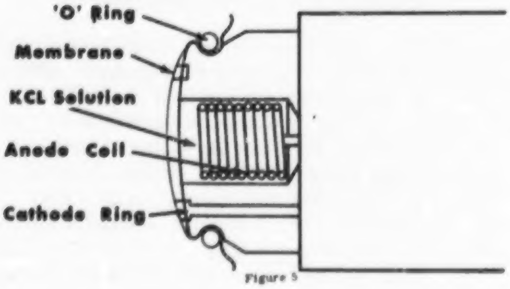

'O' Ring
Membrane
KCL Solution
Anode Coil
Cathode Ring

Figure 5

D The Model 54 YSI DO analyzer (4) is based upon the same electrode configuration but modified to include automatic temperature compensation, DO readout, and recorder jacks. A motorized agitator bottle probe is available for the Model 54 (Figure 6).

YSI Model 54 Agitator Probe

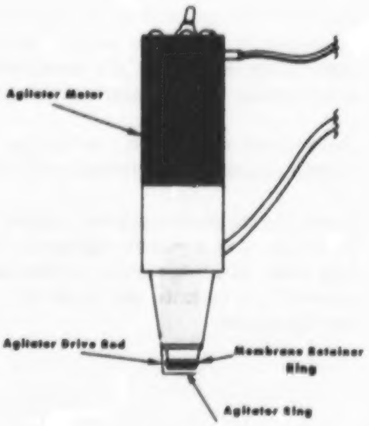

Agitator Motor
Agitator Drive Rod
Membrane Retainer Ring
Agitator Ring

Figure 6

E The Galvanic Cell Oxygen Analyzer (7, 8) employs an indicator for proportional DO signal but does not include thermistor compensation or signal adjustment. Temperature readout is provided. The sensor includes a lead anode ring, and a silver cathode with KOH electrolyte (4 molar) covered by a membrane film (Figure 7).

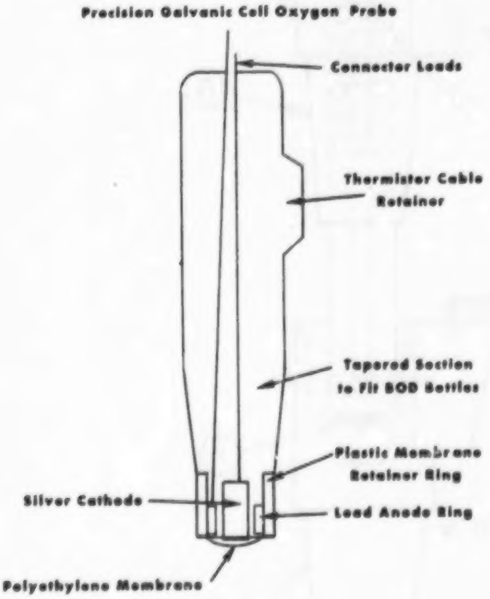

Precision Galvanic Cell Oxygen Probe
Connector Leads
Thermistor Cable Retainer
Tapered Section to Fit BOD Bottles
Plastic Membrane Retainer Ring
Silver Cathode
Lead Anode Ring
Polyethylene Membrane

Figure 7

F The Weston and Stack Model 300 DO Analyzer (8) has a galvanic type sensor with a pulsed current amplifier adjustment to provide for signal and temperature compensation. DO and temperature readout is provided. The main power supply is a rechargeable battery. The sensor (Figure 8) consists of a lead anode coil recessed in the electrolyte cavity (50% KI) with a platinum cathode in the tip. The sensor is covered with a teflon membrane. Membrane retention by rubber band or by a plastic retention ring may be used for the bottle agitator or depth sampler respectively. The thermistor and agitator are mounted in a sleeve that also provides protection for the membrane.

G The EIL Model 15 A sensor is illustrated in Figure 9. This is a galvanic cell with thermistor activated temperature compensation and readout. Signal adjustment is provided. The illustration shows an expanded scheme of the electrode which when assembled compresses into a sensor approximating 5/8 inch diameter and 4 inch length exclusive of the enlargement at the upper end. The anode consists of compressed lead shot in a replaceable capsule (later models used fine lead wire coils), a perforated silver cathode sleeve around the lead is covered by a membrane film. The electrolyte is saturated potassium bicarbonate. The large area of lead surface, silver and membrane provides a current response of 200 to 300 microamperes in oxygen saturated water at 20° C for periods of up to 100 days use (8). The larger electrode displacement favors a scheme described by Eden (9) for successive DO readings for BOD purposes.

V Table 1 summarizes major characteristics of the sample DO analyzers described in Section IV. It must be noted that an ingenious analyst may adapt any one of these for special purposes on a do-it-yourself program. The sample instruments are mainly designed for laboratory or portable field use. Those designed for field monitoring purposes may include similar designs or alternate designs generally employing larger anode, cathode, and electrolyte capacity to approach better response stability with some sacrifice in response time and sensitivity. The electronic controls, recording, telemetering, and accessory apparatus generally are semi-permanent installations of a complex nature.

ACKNOWLEDGMENTS:

This outline contains certain materials from previous outlines by D. G. Ballinger, N. C. Malof, and J. W. Mandia. Additional information was provided by C. R. Hirth, C. N. Shadix, D. F. Krawczyk, J. Woods, and others.

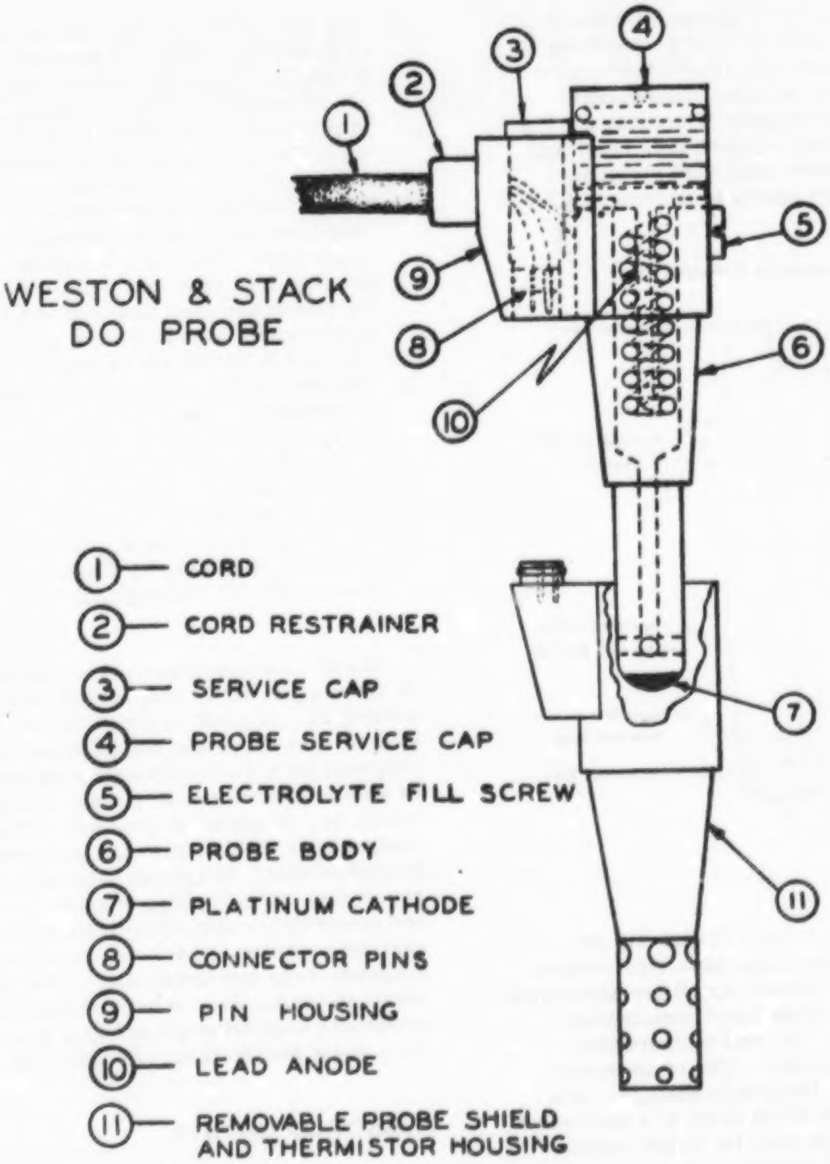
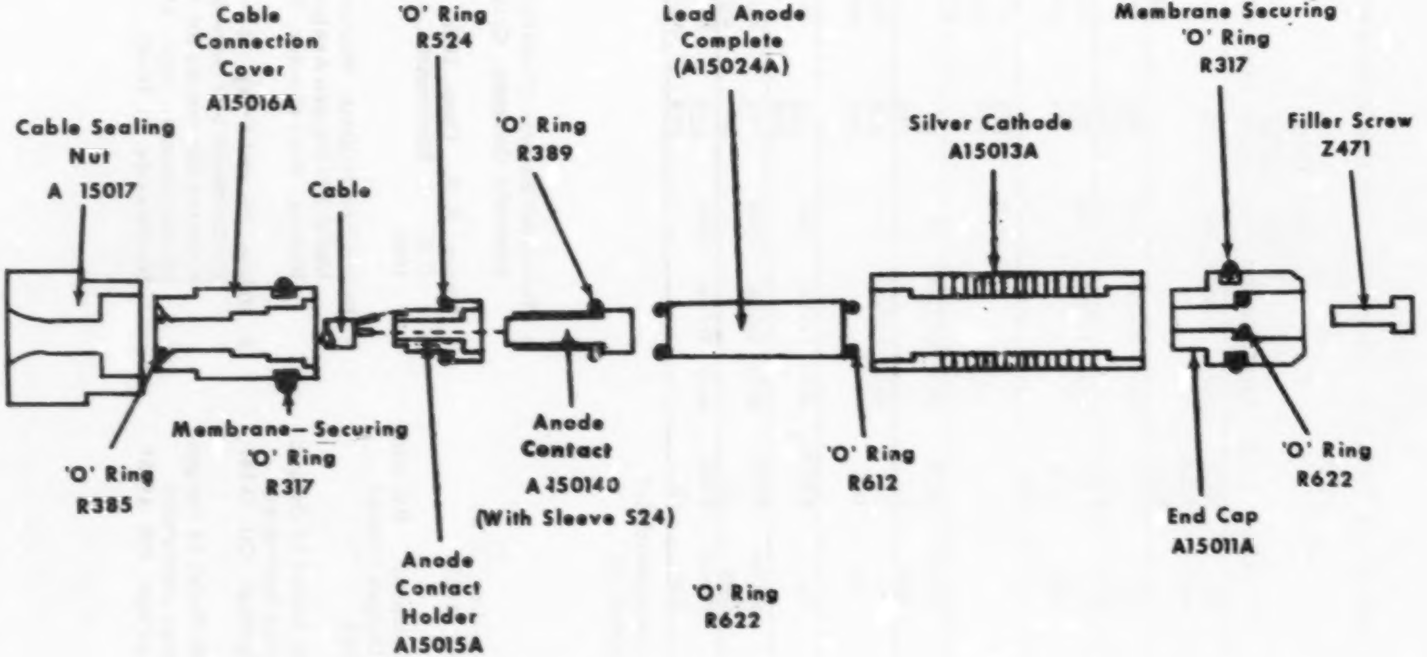

WESTON & STACK
DO PROBE
①— CORD
②— CORD RESTRAINER
③— SERVICE CAP
④— PROBE SERVICE CAP
⑤— ELECTROLYTE FILL SCREW
⑥— PROBE BODY
⑦— PLATINUM CATHODE
⑧— CONNECTOR PINS
⑨— PIN HOUSING
⑩— LEAD ANODE
⑪— REMOVABLE PROBE SHIELD AND THERMISTOR HOUSING

Figure 8

Model A15A ELECTRODE COMPONENT PARTS


Cable Sealing Nut A 15017
Cable Connection Cover A15016A
Cable
'O' Ring R524
'O' Ring R389
Lead Anode Complete (A15024A)
Silver Cathode A15013A
Membrane Securing 'O' Ring R317
Filler Screw Z471
'O' Ring R385
Membrane—Securing 'O' Ring R317
Anode Contact A 150140 (With Sleeve S24)
Anode Contact Holder A15015A
'O' Ring R622
'O' Ring R612
End Cap A15011A
'O' Ring R622

Note: Red wire of cable connects to Anode Contact Holder

Black wire of cable connects to Anode Contact

Membrane not shown E. I. L. part number T22.

Figure 9

TABLE 1

CHARACTERISTICS OF VARIOUS LABORATORY DO INSTRUMENTS

	Anode	Cathode	Elec	Type	Membr	DO Sig. Adj.	Temp. Comp. Temp. Rdg.	Accessories for which designed
Carrit & Kanwisher	silver-silver ox. ring	Pt disc	KCl KOH N/2	pol*	polyeth	no	no	Recording temp. & signal adj. self assembled
Beckman	Aq ring	Au disc	KCL gel	pol	teflon	yes	yes yes	recording
Yellow Springs 51	Ag coil	Au ring	KCl soln sat.	pol	teflon	yes	no* yes	field and bottle probe
Yellow Springs 54	"	"	"	"	"	yes	yes yes	recording field bottle & agitator probes
Precision Sci	Pb ring	silver disc	KOH 4N	galv**	polyeth	no	no yes	
Weston & Stack 300	Pb coil	Pt disc	KI 40%	galv	teflon	yes	yes yes	agit. probe depth sampler
EIL	Pb	Ag	$KHCO_3$	galv	teflon	yes	yes yes	recording
Delta 75	Lead	Silver disc	KOH 1N	galv	teflon	yes	yes no	field bottle & agitator probe
Delta 85	Lead	Silver disc	KOH 1N	galv	teflon	yes	yes yes	field bottle & agitator probe

*Pol - Polarographic (or amperometric)
**Galv - Galvanic (or voltametric)

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BIOCHEMICAL OXYGEN DEMAND TEST PROCEDURES

I OXYGEN DEMAND OF POLLUTED WATERS

Established practice includes common use of the BOD test as a tool for estimation of the bio-oxidizable fraction of surface waters or wastewaters discharged to them. Any index including a quantity per unit time such as the BOD_5 is a rate expression. The ultimate demand is more important than any one point on the progression. The results of a bottle test with minimum seeding and quiescent storage are not likely to be as high as those on the same influent in a mixing situation and abundant seed of secondary treatment or receiving waters. The BOD_5 is "a" fraction of total oxygen requirements.

A The particular technique used for BOD commonly is specified by State agencies and/or supervisors. They are required to interpret the results as obtained by laboratory testing. It is essential that the tester and the interpreters have a common understanding of what was done and how. It is highly advisable to maintain a given routine until all concerned agree upon a change.

1 Each particular routine has many undefinable factors. The particular routine is not as important as the consistency and capability with which the result was obtained.

2 This outline and Standard Methods(1) discusses several valid approaches for obtaining BOD results. Selection of "method" is not intended in this outline or in the EPA Methods Manual(2).

B The common 5-day incubation period for BOD testing is a result of tradition and cost. Initial lags are likely to be over and some unknown fraction of the total oxidizable mass has been satisfied after 5 days.

C A series of observations over a period of time makes it possible to estimate the total oxidizable mass and the fraction oxidized or remaining to be oxidized at any given time. The problem is to define the shape of the deoxygenation pattern and its limits. A fair estimate of the shape of the deoxygenation pattern is available by observations at 1, 2, or 3 days, 7 days and 14 days. Increased observations are desirable for more valid estimates of curve shape, rate of oxidation and total oxidizable mass or ultimate BOD.

D Increasing impoundment of surface waters and concurrent increases in complexity and stability of wastewater components emphasize the importance of long-term observation of BOD. The 5-day observation includes most of the readily oxidizable materials but a very small fraction of the stable components that are the main factors in impoundment behavior.

II DIRECT METHOD

A With relatively clean surface waters, the BOD may be determined by incubation of the undiluted sample for the prescribed time interval. This method is applicable only to those waters whose BOD is less than 8 mg/l and assumes the sample contains suitable organisms and accessory nutrients for optimum biological stabilization.

B Treated effluents, polluted surface waters, household and industrial wastewaters commonly require dilution to provide the excess oxygen required for the oxygen demand determination. General guidelines for dilution requirements for a given BOD range in terms of the percent of sample in BOD dilution water are:

For a 5-day BOD of
5-20 mg/l, use 25 to 100% sample

For a BOD of
20-100 mg/l, use 5 to 25% sample

For a BOD of
100-500 mg/l, use 1 to 5% sample

For a BOD of
500-5000 mg/l, use 0.1 to 1.0% sample

III PROCEDURES

A Cylinder Dilution Technique

1 Using an assumed or estimated BOD value as a guide, calculate the factors for a range of dilutions to cover the desired depletions. Those dilutions ranging from a depletion of 2 mg/1 and a residual of 1 mg/1 are most reliable. At least three dilutions in duplicate should be used for an unknown sample.

2 Into a one-liter graduate cylinder (or larger container if necessary) measure accurately the required amount of mixed sample to give one liter of diluted waste. Fill to the one liter mark with dilution water. Carefully mix. The initial DO by calculation includes IDOD (VIII) a determined initial does not. Both are essential to estimate significance of IDOD. Entrapment of air bubbles during manipulation must be avoided.

3 Siphon the mixture from the cylinder into three 300 ml glass stoppered bottles, filling the bottles to overflowing.

4 Determine the DO concentration on one of the bottles by the appropriate Winkler modification and record as "Initial DO".

5 Incubate the two remaining bottles at 20°C in complete darkness. The incubated bottles should be water-sealed by immersion in a tray or by using a special water-seal bottle.

6 After 5 days of incubation, or other desired interval, determine the DO on the bottles. Average the DO concentration of the duplicates and report as "Final DO".

B Direct Dilution Technique

1 It may be more convenient to make the dilution directly in sample bottles of known capacity. A measured volume of sample may be added (as indicated in A-1) and the bottle filled with dilution water to make the desired sample concentration for incubation. In this case, the sample must be precisely measured, the bottle carefully filled, but not overfilled, and the bottle volumes comparable and known. Precision is likely to be poorer than for cylinder dilution.

2 Continue the procedure as in A-4, 5, and 6.

C Seeded Cylinder Dilution Technique

1 Many wastewaters may be partially or completely sterile as a result of chlorination, effects of other toxic chemicals, heat, unfavorable pH or other factors detrimental to biological activity. Validity of the BOD result depends upon the presence of organisms capable of prompt and effective biodegradation and favorable conditions during the particular test. Correction of the cause resulting in sterilization must be corrected by adjustment, dilution, etc., prior to reinoculation to achieve meaningful BOD data. Receiving water, biologically treated effluents, and soil suspensions are a good source of organisms likely to be adapted for stabilization of wastewaters. Untreated wastewaters provide numerous organisms but are likely to contain nutrients contributing to excessive seed corrections and may require appreciable time for adaptation before test waste oxidation becomes significant.

2 The amount of added inoculant must be determined by trial. The concentration added should initiate biochemical activity promptly but should not exert enough oxygen demand to unduly reduce the oxygen available for sample requirements.

3 Estimate the sample concentration desired in accordance with A-1 and C-2 and add the sample aliquot to the dilution cylinder.

4 Add approximately half of the required amount of dilution water to the sample and mix. This is necessary to assure that the concentrated waste does not exert a toxic effect on the seed organisms.

5 Measure a suitable aliquot of seed into the bottle or cylinder and fill with dilution water. Mix the combined sample, seed and dilution water without excessive air entrainment.

6 Continue as in III-A steps 4, 5, and 6.

IV INTERPRETATION OF RESULTS

Standard Methods(1) includes a calculation section that is valid and concise. Preceding it are details of reagent preparation and procedures for the test. These will not be reprinted here. This section considers certain items that may cause concern about the validity of results unless they are carefully considered and controlled.

A The initial DO of the BOD test obviously should be high. The method of attaining a high DO can trap the analyst.

1 Aeration of dilution water is the most commonly considered treatment. This technique does produce a high DO but it is a treacherous ally.

a Dirty air passing through clean dilution water can produce clean air and dirty water. This is a simple air-washing operation. Filtering the entering air stream may remove brickbats and 2 x 4's, but filters tend to pass organic gases, fine aerosols, and particulates.

b A stream of air passing through water tends to cool the water by evaporation 1 to 3°C below ambient temperature. The cooled liquid picks up more DO than it can hold at ambient temperature. The physical loss of oxygen may produce an erroneously high depletion value for a determined initial DO, or a low depletion on a calculated initial DO. Erroneous blanks are a particular concern. The dilution water temperature/DO shift is critical.

2 Raising DO by allowing the sample to equilibrate in a cotton-plugged bottle for 2 or 3 days permits oxygenation with minimum air volume contact.

3 Shaking a partially filled bottle for a few seconds also oxygenates with minimum opportunity of gas washing contamination, supersaturation, or temperature changes.

B Seeding always is a precarious procedure but a very necessary one at times. Often the application of seed corrections is a "________if you do, _______if you don't" situation. Hopefully, seed corrections are small because each individual biological situation is a "universe" of its own.

1 Unstable seeding materials such as fresh wastewater have "seed" organisms characteristic of their origin and history. Saprophytes resulting in surface water stabilization may be a small fraction of the population. Reactable oxygen-demanding components produce excessive demands upon test oxygen resources.

2 A seed containing viable organisms at a lower energy state because of limited nutritional availability theoretically is the best available seed source. An organism population grown under similar conditions should be most effective for initiating biochemical activity as soon as the nutrient situation favors more activity. The population should not be stored too long because organism redistribution and die-out become limiting. This type of seed would most likely be found in a surface water or a treatment plant effluent with a history of receiving the particular material under consideration.

3 Seed sources and amounts can only be evaluated by trial. Different seed sources and locations require checkout to determine the best available material from a standpoint of rapid initiation of activity, low correction, and predictable high oxygen depletion under test.

C Chlorination and BOD results fundamentally are incompatible. Chlorination objectives include disinfection as the number one goal. Chlorine is notoriously non-specific in organism effects. Chlorine acts like an oxidant in the DO determination. Test organisms are less suitable for activity than they were before chlorination. Nutrients may be less available after chlorination. Certainly the conditions are less suitable for biological response after chlorination. Dechlorination is feasible with respect to the oxidizing power of chlorine, but many organic chlorine compounds that do not show strong oxidizing action still have toxic effects on biologic response.

Numbers are obtainable after dechlorination and reseeding. The meaning of these numbers is obscure. At least two states (New York and New Jersey) specify BOD's before chlorination only.

V PRECISION OF THE BOD TEST

A The DO test precision often has been used to suggest precision of the BOD result.

DO precision is a relatively minor and controllable factor contributing to BOD results. Other factors such as organism suitability, members, adaptation and conditional variables are much more difficult to control or to evaluate.

B The Analytical Reference Service report on Water Oxygen Demand, July, 1960 (Sample type VII) included the results of seeded samples of glucose-glutamic acid BOD results from 34 agencies on 2, 3, 5 and 7 day incubations.

The relative geometric standard deviation (average) was 19% on 2% sample and 24% on 1% sample concentrations. Rate coefficients ranged from 0.10 to 0.27 with a median of 0.16 from 21 different laboratories that participated in rate studies.

VI ALTERNATE BOD TECHNIQUES

Reaeration methods are becoming increasingly popular in order to approach more nearly the actual waste concentration in the receiving water. It is common to obtain "sliding" BOD results related to the concentration of waste in a series of dilutions of the same sample. This may result from greater possibilities for toxic effects at higher concentrations, or to a different selection of organisms and change in oxidation characteristics at low concentrations of sample. The most reliable estimate of stream behavior is likely to be from that dilution closest to the wastewater dilution in the receiving water.

A Reaeration can be accomplished by the usual series techniques by dumping all of the remaining sealed bottles into a common container when the residual DO reaches about 1.0 mg/1. After reoxygenation, the remaining bottles are refilled and a new initial DO determined. Subsequent dissolved oxygen depletions are added incrementally as a summation of the total oxygen depletion from the start of the test. If necessary, the reaeration technique may be performed several times but at a sacrifice of double DO determinations for each day on which reaeration occurs.

B Special methods of reaeration have evolved to minimize the extra manipulation for reaeration of individual sample dilutions.

1 Elmore Method

A relatively large volume of the sample is stored in an unsealed bottle. Small bottles are withdrawn in sets of 3 or more, sealed, incubated, and the DO determined at appropriate intervals. When the DO concentration in the smaller bottles reaches 1.0 mg/1, a new set is withdrawn from the large unsealed bottle, after reoxygenation if necessary.

2 Orford Method

The deoxygenation is carried out in a large sealed jug from which samples for DO are withdrawn at appropriate intervals. To maintain the waste level and a sufficient DO in the jug, additional waste is added from a second open container. See diagram.

C Excess oxygen may be provided by oxygenation with commercial oxygen instead of with air to increase the initial oxygen content for incubation while limiting the number of dilutions or reaeration steps. When oxygen is used in place of air the oxygen saturation in water at 20°C is about 40 mg/1 instead of 9 mg/1. Limited results are available hence the analyst must verify his technique. The DO tends to decrease as soon as the bottle is opened hence, about 35 mg/1 of oxygen content is the top of the practical working concentration. There has been no evidence that the biota is inhibited by the higher oxygen content with respect to BOD progression.

D Reaeration or Oxygenation Advantages and Limitations.

1 Reaeration expands the range of BOD results obtainable directly at field concentrations, but is not advisable for applications when the sample BOD exceeds 50 mg/1.

2 Dilution water problems are eliminated, to the extent that the stream sample may be tested without dilution.

3 Incubator storage space becomes a real problem for multiple sample routine.

VII Dissolved oxygen electrodes, polarographic and others, are feasible for use in BOD determinations, often making it possible to make an estimate of DO or BOD when sample interference prevents a valid Winkler DO determination.

Electronic probe DO makes it possible to determine many successive DO's at different time intervals on the same bottle with negligible sample loss. Reaeration or extended time series, therefore, are more feasible.

Another outline in this series describes response of reaerated BOD_5 with electronic DO probes.

A It is the responsibility of the analyst to evaluate:

1 Applicability of the specified technique and sample.

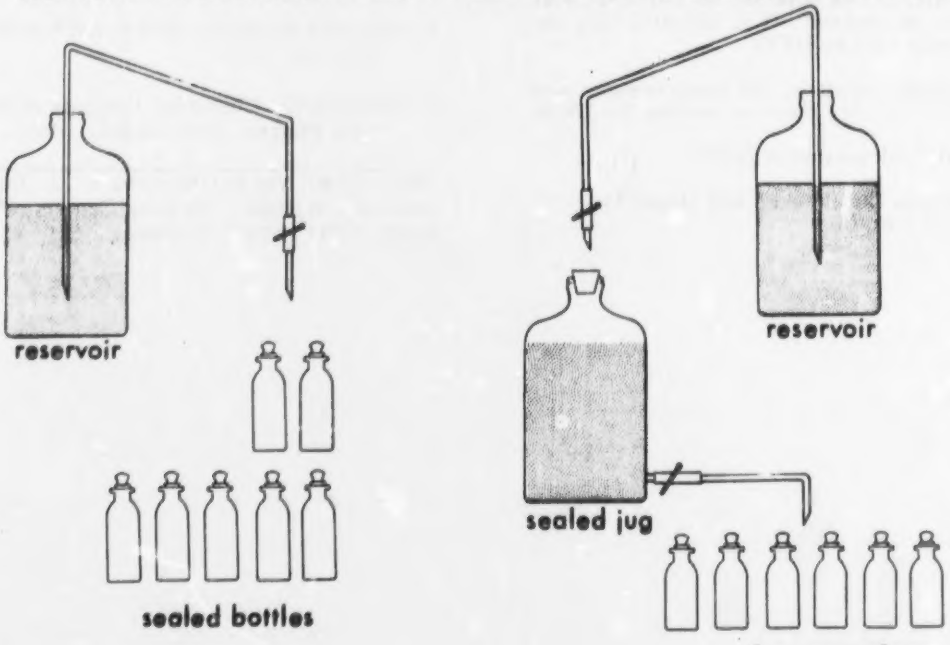
2 To determine requirements for mixing and possible thermal effects while mixing in terms of instrument response and biochemical reaction.

3 To evaluate long-term calibration or standardization and their effects upon precision and accuracy of the BOD result.

VIII IMMEDIATE DISSOLVED OXYGEN DEMAND (IDOD)

Immediate dissolved oxygen demand includes dissolved oxygen utilization requirements of substances such as those in I-A-3. An arbitrary period of 15 min. has been selected to distinguish IDOD from BOD.

REAERATION METHODS FOR B.O.D. DETERMINATION



ELMORE METHOD **ORFORD METHOD**

A The IDOD is an apparent response as indicated by a specified technique. Since DO titration is based upon iodine titration, any factor that causes I_2 response different from that produced by the reaction of KI and molecular oxygen confuses the IDOD determination.

B IDOD Determination

1 The IDOD determination includes the determination of DO on a sample and dilution water separately. A waste likely to have a significant IDOD is unlikely to show a DO.

2 According to mixing theory, it should be possible to calculate the DO of any definite mixture of the sample and dilution water from the DO of component parts and their proportion. (See IV. E. 1).

3 The same relative proportions of sample and dilution water should be mixed without air entrainment and the DO determined after 15 minutes.

4 Any difference between the calculated initial DO as obtained in VIII-B-2, and the determined DO in VIII-B-3 may be designated as IDOD.

5 Sample aeration, DO interference, and other factors confuse results for IDOD.

C Sample Calculation of IDOD

1 Sample DO checked and shown to be 0.0 mg/l

Dilution water DO found to be 8.2 mg/l

Assume a mixture of 9 parts of dilution water and 1 part (V/V) of sample.

Calculated DO =

$1 \times 0 = 0$

$9 \times 8.2 = 73.8$

10 parts of the mixture contain 73.8/10 or 7.4 mg DO/l. Note that mixing has reduced the DO concentration because the original amount is present in a larger package.

2 The mixture described in C-3 was held for 15 minutes and the DO determined was 4.3 mg/l.

$$\text{IDOD} = \text{DO}_{\text{calc}} - \text{DO}_{\text{detm}} \times \frac{100}{\%\ \text{sample used}}$$

$$= 7.4 - 4.3 \times 10$$

$$= 31 \text{ mg IDOD/l}$$

Bibliography

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BOD DETERMINATION - REAERATED BOTTLE PROBE TECHNIQUE

I INTRODUCTION

A Customary dilution technique has certain limitations with respect to the BOD determination such as a prior commitment on sample dilutions to be used, number of bottles to be included to permit Winkler DO determinations to be made throughout a predetermined test interval, (with sample destruction for each DO test), possibility for anomalous effects due to dilution water, dilution, or inconsistent response between test bottles.

B DO probe technique offers the advantages of nondestructive DO testing, possibilities of adjusting routine according to sample behavior during test, and retaining the sample with minor losses for long term observation (if desired) and for supplementary tests at the end of the BOD test interval.

Note: Use of the probe results in a loss of about 1/2 ml of each 300 ml sample. Use dilution water with a glass rod or bead to bring the sample volume back to 300 ml for further testing.

C This test was performed in triplicate on the same sample at 100% concentration with reaeration as needed to illustrate results obtainable.

II PROCEDURE

A Sample

Final effluent (catch sample at 1100 hours) of the Advanced Waste Treatment Research Activated Sludge (Unit B) Sanitary Engineering Center Experimental Wing (September 3, 1970). One hundred percent concentration.

B DO Probe Calibration

The probe was calibrated daily in air saturated tap water versus the azide modification of the iodometric titration. A replicate test bottle of the titrated sample was retained for initial probe adjustment, if necessary, and to recheck sensor response at the end of the use period. Zero sensor response in cobalt treated sulfite solution was checked at three day intervals. Electronic response and battery condition were checked daily.

C Reaeration

1 When the DO test indicated 1.0 mg DO/liter or appeared likely to reach that point prior to the next test reading the test bottles were reaerated and a new initial DO was obtained.

2 An adapter was inserted into the neck of the sample bottle indicating low DO and an empty bottle inserted on the opposite end. The combination was shaken vigorously, while in an inverted position to allow the transfer of sample to the empty bottle; immediately after transfer the combination was reinverted, shaken as before and sample returned to the original bottle.

3 The sample was allowed to stand for at least five minutes to allow entrained air to rise (generally formed a froth ring). The froth ring was raised into the neck of the bottle by displacement with about 1/2 ml of dilution water. It usually was necessary to tilt the bottle slightly and roll it to sweep fine air bubbles off the shoulder of the bottle and into the neck. After careful reinsertion of the DO sensor these bubbles were displaced by tipping the assembly and discarding contents of the BOD bottle lip containing the frothy residue.

4 It is recognized that surface active materials and possibly other components would concentrate in the discarded froth. It would be possible to limit this effect

by allowing a longer time for the froth to break--say 15 to 30 minutes. This was not attempted for this demonstration.

D No attempt was made to determine DO at any regular time interval. Observation time is recorded for each test on a 24-hour clock basis with zero time at midnight.

E Results are recorded in tabular form including the date (Column 1), time in hours (2), sample temperature (3), hours of incubation (4), and the triplicate sample data. For each of the samples the observed DO, the change since the last observation (ΔDO) and the summation of all the DO depletions observed during the incubated interval are recorded as Σ ΔDO. A bold face line in the tabulated data in the DO column indicates DO before reaeration; the number below the line indicates DO after reaeration to be used as a new initial for the next observation.

F Near the end of the fifth day of incubation (116 hours) one of the triplicates (no. 3) was not reaerated to check the effect of complete depletion of oxygen. It was reaerated on the following day and thereafter.

G The results plotted in graphic form are presented following the BOD tabular data.

H The results of a similar respiration test on mixed liquor from the same activated sludge units are tabulated to show the effects of different types of feed on DO depletion (respiratory activity). In this case, time is in minutes, DO is in mg/l and ΔDO/minute also is in mg/l. The first test in Table 2 represented 100 ml of return sludge plus plant effluent to fill the bottle. Approximately one percent nutrient agar solution was added by syringe (1.0 ml) to produce the response noted in the second series; one ml of five percent mercuric chloride produced the effects in series 3. A new replicate sample (100 ml sludge) and plant influent to fill the bottle produced the results in series 4.

III SUMMARY

A Table 1 shows that it is possible to obtain consistent results using a DO probe plus reaeration for BOD technique. The major requirement is to carefully calibrate the DO instrument and sensor on a daily basis. It is not recommended to reaerate as many times as found necessary here. It could have been diluted at any time since the sample was available. Had the BOD response at five days been substantially complete only two reaerations would have been necessary. However, since the sample was working into second stage BOD it proceeded to react accordingly. The oxygen demand of 15 mg/liter at five days increased to 30 mg/liter in seven days and reached 45 mg/liter in ten days. The sample that was allowed to deplete on the fifth day slowly recovered but by the twelfth day or thereafter equaled or exceeded the BOD of the samples with residual DO at all times. This technique requires much less incubator space, time and manipulation with an added advantage of retaining the sample for adjustment or extended observation. The results do not depend upon a preconceived guestimate which may or may not fit the situation.

B Table 2 indicates the possibility for estimating feed acceptability in an activated sludge treatment plant. On many occasions an inquiry from an industrial plant, a different type of inflow or perhaps a new plant requires a decision regarding effects at the treatment plant. A respiration test by probe technique offers an opportunity to rate the situation within ten minutes after probe calibration. A test of sludge and effluent oxygen demand gives an estimate sludge respiratory activity now. When the same sludge is subjected to a new feed of an acceptable nature respiratory activity rises as in series 2. If the feed happened to be highly toxic as in series 3 (mercuric chloride) respiratory activity stops--

obviously a dead or severely shocked condition. A replicate sludge (Series 4) with the regular plant influent shows a prompt increase in activity. Oxygen requirements, permissible load ratio, acceptable feed to sludge ratios (return sludge adjustment) all may be estimated on the basis of DO tests related to overall plant performance.

C The graphic of BOD versus time includes the COD--an estimate of first stage oxygen demand and the TKN for the composite effluent sample. If the total Kjeldahl nitrogen (TKN) is multiplied by its oxygen equivalent (4.57) then the COD plus TKN times 4.57 gives an estimate of ultimate oxygen demand (138 mg/l). The twenty day BOD was about 55 × 100/138 or forty percent of this value. The effluent sample obtained at 1100 hours is unlikely to contain a significant portion of the high load period considering the primary, aerator and secondary clarifier detention. Also the COD and TKN may have included materials that were chemically oxidized but gave a poor response to biological oxidation. The BOD gives the rapid respiratory oxygen demand. COD plus the oxygen equivalent of N (on the same sample) gives a quick estimate of potential ultimate demand.

This outline was prepared by F. J. Ludzack, Chemist, National Training Center, DTTB, MDS, WPO, EPA, Cincinnati, OH 45268.

TABLE 1
BOD Tabulated Results - Reaerated Sample; Probe DO

9/3/70 100% Sample

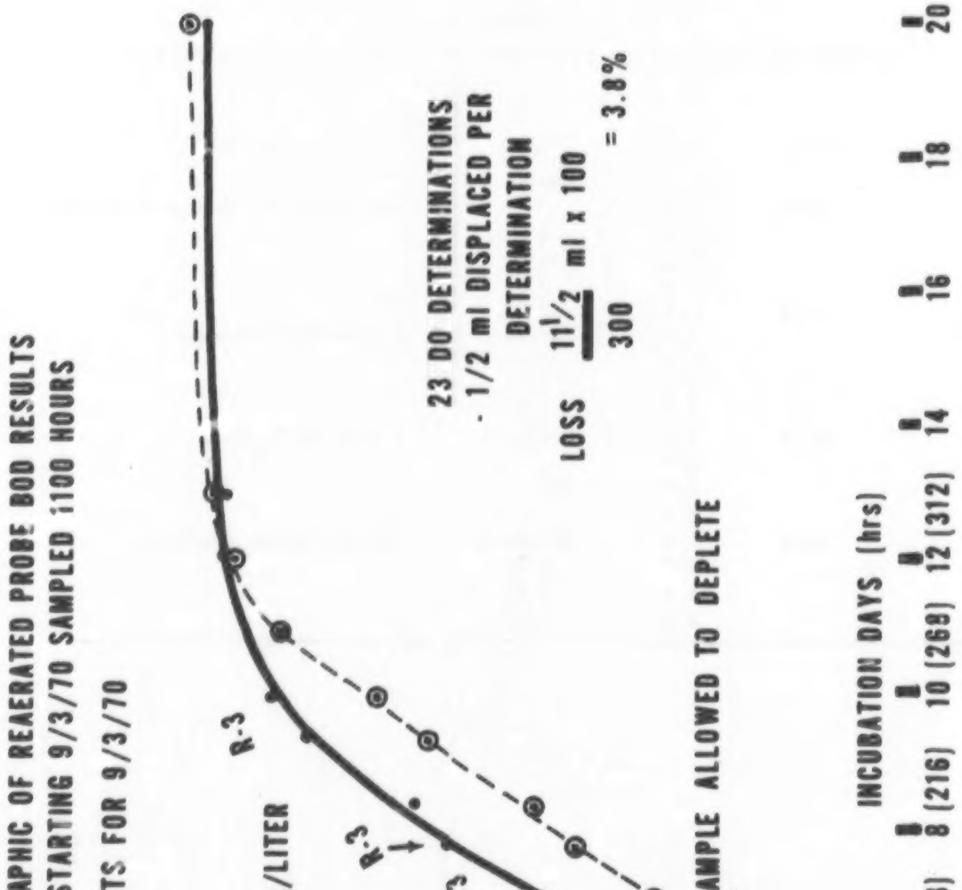
				Sample 1			Sample 2			Sample 3		
Date	Time	T° C	Hrs. Incub	DO	ΔDO	ΣΔDO	DO	ΔDO	ΣΔDO	DO	ΔDO	ΣΔDO
9/3/70	1340	24.0	0	6.7			6.7			6.8		
9/3/70	1355	24.0	0.25	6.7	-		6.7	-		6.8	-	
9/3/70	1620	22.0	2.6	6.5	0.2	0.2	6.5	0.2	0.2	6.6	0.2	0.2
9/4/70	1010	20.2	20.5	4.9 8.2	1.6	1.8	4.7 8.3	1.8	2.0	4.8 7.9	1.8	2.0
9/4/70	1600	20.6	26.3	7.4	0.8	2.6	7.5	0.8	2.8	6.9	1.0	3.0
9/6/70	1340	19.5	72	1.0 8.1	6.4	9.0	1.5 8.1	6.0	8.8	1.1 7.4	5.8	8.8
9/8/70	0940	19.8	116	0.6 8.6	7.5	16.5	0.5 7.6	7.6	16.4	0.4	7.0	15.8
9/9/70	1235	20.0	143	1.1 8.2	7.5	24.0	1.1 8.2	6.5	22.9	0.0 7.6	0.4	16.2
9/10/70	1200	20.0	166	1.0 8.2	7.2	31.2	1.2 8.6	7.0	29.9	2.0 8.0	5.6	21.8
9/11/70	0800	20.0	186	1.2 8.4	7.0	38.2	1.1 8.3	7.5	37.4	2.0 8.5	6.0	27.8
9/11/70	1400	20.0	192	5.0 8.1	3.4	41.6	5.3 8.4	3.0	40.4	5.7 8.6	2.8	30.6
9/12/70	2035	20.0	222	0.5 8.2	7.6	49.2	0.6 8.2	7.8	48.2	0.4 8.2	8.2	38.8
9/13/70	1130	20.0	238	6.3 8.3	1.9	51.1	3.8 8.4	4.4	52.6	4.6 8.3	3.6	42.4
9/14/70	1200	20.0	262	7.0	1.3	52.4	6.9	1.5	53.1	0.9 8.3	7.4	49.8
9/15/70	1340	19.6	288	5.7	1.3	53.7	6.2	0.7	53.8	4.5 8.2	3.8	53.6
9/16/70	1200	19.3	310	5.1	0.6	54.3	5.8	0.4	54.2	7.2	1.0	54.6
*9/20/70	1240	21.6	460	3.8	1.3	55.6	4.6	1.2	55.4	4.9	2.3	56.9

* Incubator power off

TABLE 2

ACTIVATED SLUDGE RESPIRATION DATA DO PROBE TECHNIQUE

Time Min	Temp	DO	ΔDO	Sample
			Series 1	
0	24°	7.2		100 ml Return Sludge & Effluent
1		6.6	0.6	
2		6.2	0.4	
3		5.6	0.6	
4	24.5	5.1	0.5	
0		4.7	Series 2	+ 1 ml Nutrient agar
1		3.8	0.9	
2		2.7	1.1	
3		1.7	1.0	
0	21.8	4.7	Series 3	+ 1 ml $HgCl_2$ Soln
1		4.8		
2		4.7	Nil	
3		4.7		
0	24.2	5.9	Series 4	100 ml Sludge + Influent
1		4.6	1.3	
2		3.3	1.3	
3		2.0	1.3	


GRAPHIC OF REAERATED PROBE BOD RESULTS
STARTING 9/3/70 SAMPLED 1100 HOURS
COMPOSITE SAMPLE RESULTS FOR 9/3/70
COD-39 mg/LITER
TKN-15 mg/LITER
ULTIMATE DEMAND 138 mg/LITER
ΣΔ DO - BOD SAMPLE DEPLETION Mg/l
50
45
40
35
30
25
20
15
10
5
R-3
R-3
R-3
R-3
R-3
R-2
R-3
R-3
SAMPLE ALLOWED TO DEPLETE
23 DO DETERMINATIONS
- 1/2 ml DISPLACED PER
DETERMINATION
LOSS $\frac{11\frac{1}{2} \text{ ml} \times 100}{300} = 3.8\%$
2(72)
4 (120)
6 (168)
8 (216)
10 (269)
12 (312)
14
16
18
20
INCUBATION DAYS (hrs)

MATHEMATICAL BASIS OF THE BIOCHEMICAL OXYGEN DEMAND (BOD) TEST

Part 1

I FUNDAMENTAL CONCEPTS

For a number of years, the oxidation of organic waste substances in surface waters has been under investigation. The first reported observation of oxygen depletion was on the Seine River below Paris (1877). Other studies followed in Germany, England and the U.S. Certain fundamentals are now universally accepted. These are:

A Dissolved oxygen in the water is reduced during stabilization of the organic material.

B As long as dissolved oxygen is present, the rate of oxidation is independent of the actual amount of oxygen available.

C The type and numbers of biological forms present is an important factor.

D Measurement of changes in oxygen content can be related to quantity and character of oxidizable organic matter.

II FIRST ORDER RATE CONCEPT

In order to illustrate the mathematical relationships in the BOD reaction, assume the following laboratory observations:

A A set of replicate bottles is filled with river water and sealed so that outside air is excluded.

B Each day, one of the bottles is analyzed for DO content, and the results tabulated. (See Table 1.)

It will be noted that on each successive day, the DO concentration is less than the day before. That is, oxygen is being consumed by biological or chemical action in the water. The oxygen residual when plotted against time forms the deoxygenation curve (Figure 1).

The oxygen demand or BOD curve is represented by the summation of observed oxygen depletions vs. time (Figure 2). This

Table 1.

Days	DO	Oxygen depletion	
		Per day	Cumulative
0	9.2	0	-
1	7.4	1.8	1.8
2	5.8	1.6	3.4
3	4.6	1.2	4.6
4	3.7	0.9	5.5
5	2.9	0.8	6.3
6	2.3	0.6	6.9
7	1.8	0.5	7.4
8	1.5	0.3	7.7
9	1.2	0.3	8.0
10	0.9	0.3	8.3

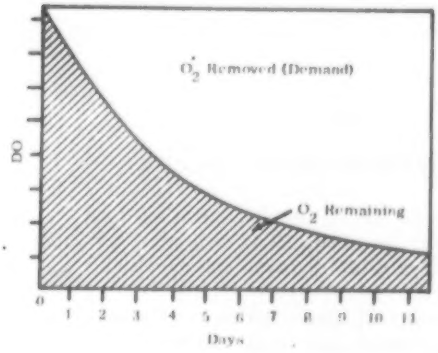


Figure 1

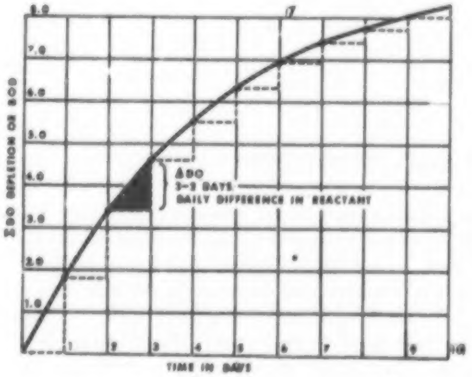


Figure 2. INTEGRAL BOD CURVE

is an inverted representation of the deoxygenation curve. Inclusion of the daily equilavents of oxygen demand in Figure 2 shows that increasingly smaller amounts of oxygen normally are used during each successive day.

If the reaction follows a 1st-order rate system, a constant percentage of the oxygen present at the beginning of each day will be used during that day. Therefore, the rate coefficient (K in nat. log. or k_1 in $\log_{10}$) is constant from day to day. $K_1 = 2.3\ k_1$.

Similarly, the organic matter present in the sample is being oxidized, so there is progressively less oxidizable material present each successive day. The relationship between oxygen demand and the amount of oxidizable material present can be stated as follows: The oxygen demand per unit time is proportional to the amount of unoxidized material present. Streeter and Phelps$^{(1, 2)}$ stated the concept as - the rate of biochemical oxidation of organic matter is proportional to the concentration of unoxidized substance, measured in terms of oxidizability. Such a rate is termed a First Order Reaction Rate. The same authors also stated that there is no logical reason to expect one rate coefficient but it may appear so becau of crude m[illegible]surement and the effects of many ind[illegible]ual oxidation systems.

The curve as shown in Figure 2 is a typical BOD curve. When interpreted in light of the fundamentals previously discussed, it is apparent that:

1 With organic materials which are easily oxidized, the reaction proceeds rapidly, nearing stabilization in a few days. The curve is therefore steep, rapidly approaching a maximum.

2 As oxidation nears completion the BOD curve will approach a limit or maximum value that can be represented by a line above the time axis and parallel to it. This line represents the ultimate oxygen demand (L) for the sample and conditions of the test. The curvature of the BOD line as it approaches the maximum is a function of the rate of oxidation.

3 The BOD test commonly is applied for samples containing mixed components each of which may differ in availability as a nutrient. The population of organisms generally contains many varieties. A progression of varieties occurs from those favored by an excess of initial nutrients to those favored by cell mass and eventually to those tolerating a low available energy level.

4 This type of system may have apparent characteristics of 1st order reaction mechanisms for limited periods of time. It is likely that two or more 1st order mechanisms may be apparent if observation time, nutrients and conditions are appropriate. The data also may be interpreted as a zero order, 2nd order or multiple order reaction mechanism. It is not always possible to prove reaction order nor is it essential to do so. The main objectives are to be able to estimate the ultimate BOD, the amount of BOD remaining after a given time interval and to obtain reasonable agreement among observed and calculated data. The first order reaction concept provides "a" means to meet the need without implying that the reactions are necessarily 1st order or that it is the only means of approach.

III BOD EQUATION

Using the typical BOD reaction curve, it is possible to develop equations expressing the various relationships. Labeling the coordinates as in Figure 3,

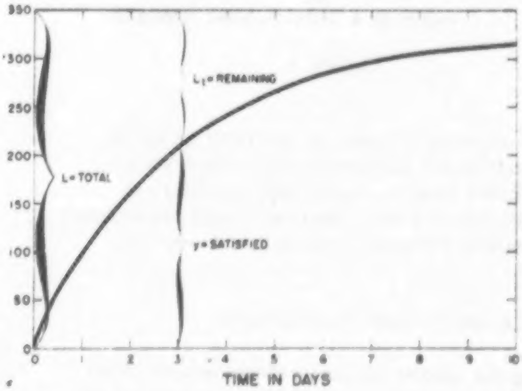


Figure 3

t = time in days

L = ultimate demand

L_t = demand remaining at time t

y = demand satisfied at time t

then:

$\frac{L_t}{L}$ = fraction of L remaining at time t

$\frac{y}{L}$ = fraction of L oxidized at time t

The relationships may be expressed as a differential equation with respect to "t"

$$\frac{dL}{dt} = -KL \qquad (1)$$

where K is a rate coefficient for deoxygenation as a $\log_e$.

$$\mathrm{Ln}\,\frac{(L-y)}{L} = -Kt \qquad (2)$$

changing to $\log_{10}$

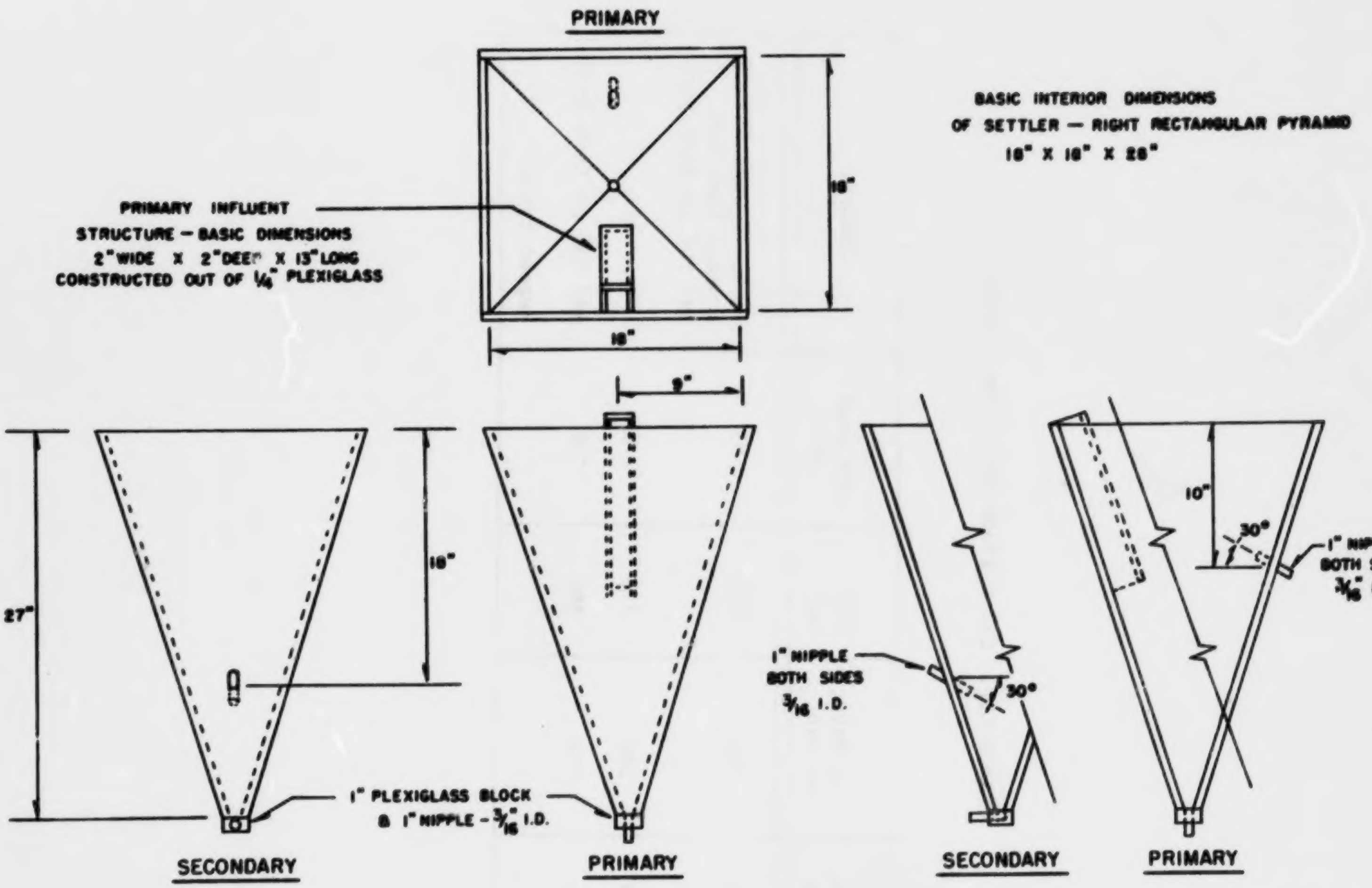
$$\mathrm{Log}_{10}\,\frac{(L-y)}{L} = -kt \qquad (3)$$

and:

$$\frac{(L-y)}{L} = 10^{-kt}$$

Table 2
Equivalents in the BOD Equation

BOD remaining at time t	$L-y$	L_t	
Fraction of BOD remaining	$L-y/_L$	$L_t/_L$	10^{-kt}
Conversion of $\log_e$ to $\log_{10}$	K	2.3k	
Fraction of BOD satisfied	$1-\frac{L-y}{L}$	$1-\frac{Lt}{L}$	$1-10^{-kt}$

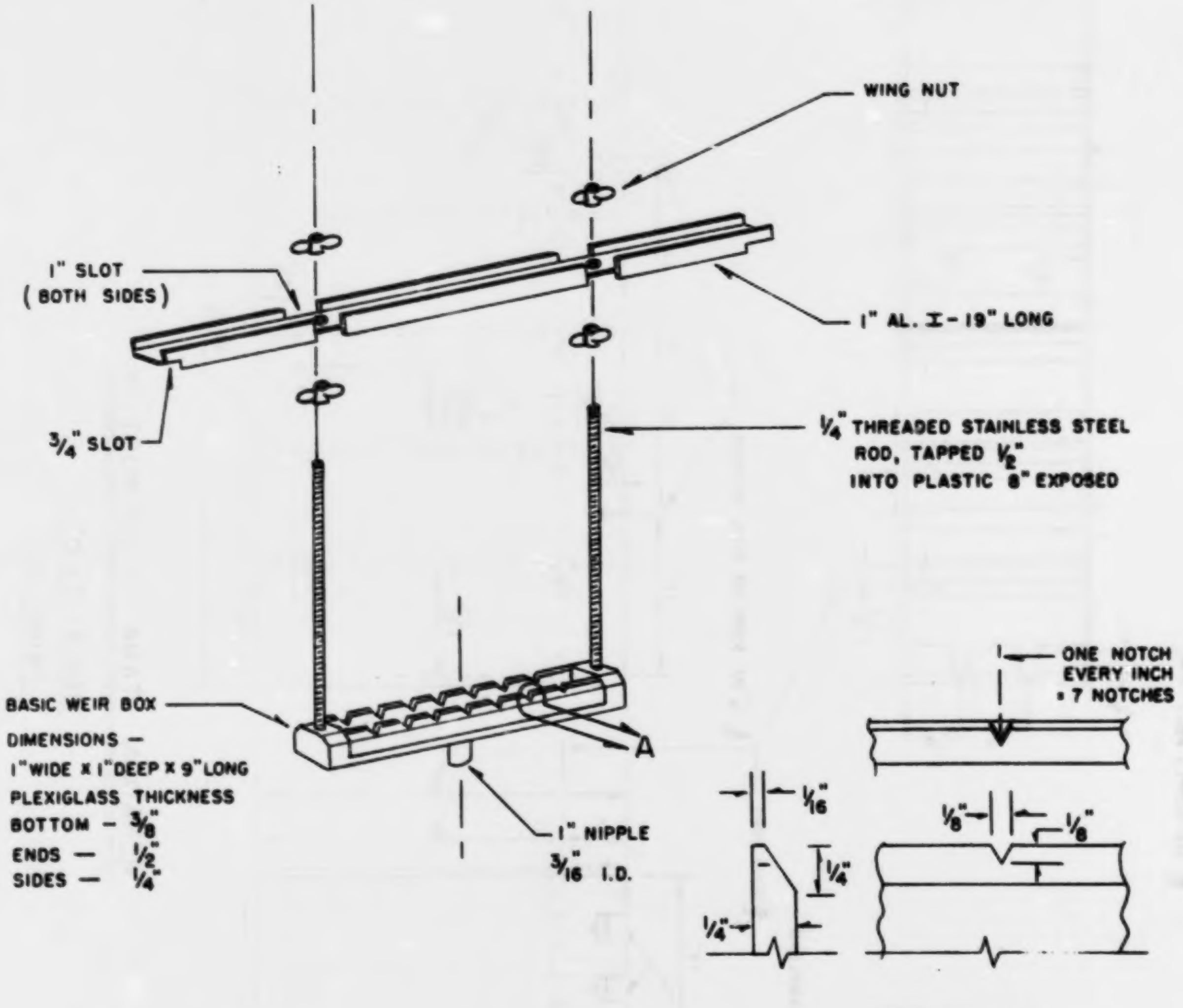

PRIMARY
BASIC INTERIOR DIMENSIONS
OF SETTLER — RIGHT RECTANGULAR PYRAMID
18" X 18" X 28"
PRIMARY INFLUENT
STRUCTURE — BASIC DIMENSIONS
2" WIDE X 2" DEEP X 13" LONG
CONSTRUCTED OUT OF 1/4" PLEXIGLASS
18"
18"
9"
27"
18"
10"
30°
1" NIPPLE
BOTH SIDES
3/16" I.D.
1" NIPPLE
BOTH SIDES
3/16 I.D.
30°
1" PLEXIGLASS BLOCK
& 1" NIPPLE - 3/16" I.D.
SECONDARY
PRIMARY
SECONDARY
PRIMARY

NOTE: ALL FORMS PLEXIGLASS - 1/2" THICK
UNLESS OTHERWISE NOTED

SETTLER CONSTRUCTION

SCALE: 1" = 10"

FIGURE 1


WING NUT
1" SLOT
(BOTH SIDES)
1" AL. I - 19" LONG
3/4" SLOT
1/4" THREADED STAINLESS STEEL
ROD, TAPPED 1/2"
INTO PLASTIC 8" EXPOSED
BASIC WEIR BOX
DIMENSIONS —
1" WIDE x 1" DEEP x 9" LONG
PLEXIGLASS THICKNESS
BOTTOM — 3/8"
ENDS — 1/2"
SIDES — 1/4"
A
1" NIPPLE
3/16" I.D.
ONE NOTCH
EVERY INCH
= 7 NOTCHES
1/16"
1/4"
1/4"
1/8"
1/8"

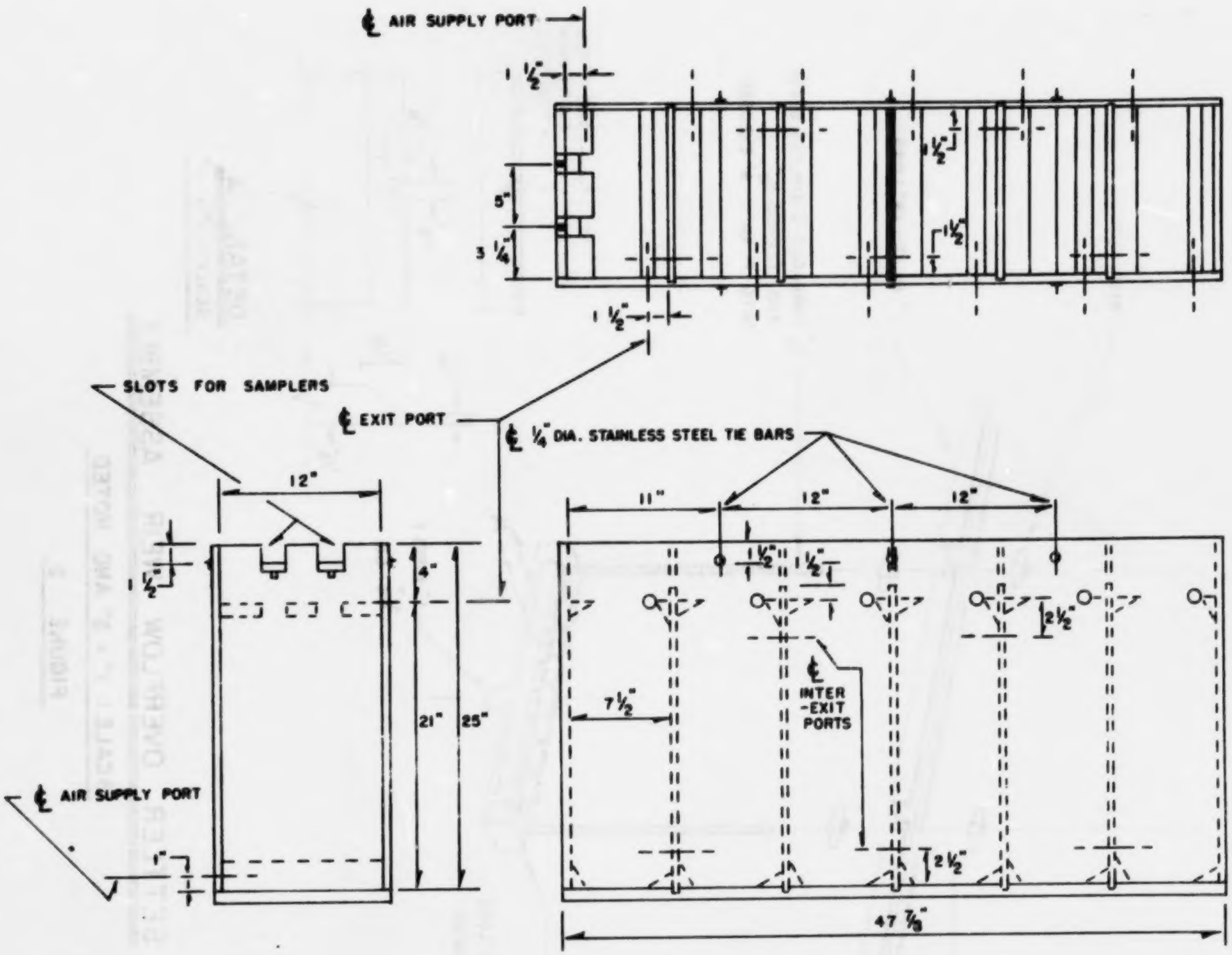
DETAIL A

SCALE : 1" = 1"

SETTLER OVERFLOW WEIR ASSEMBLY

SCALE : 1" = 5" AND NOTED

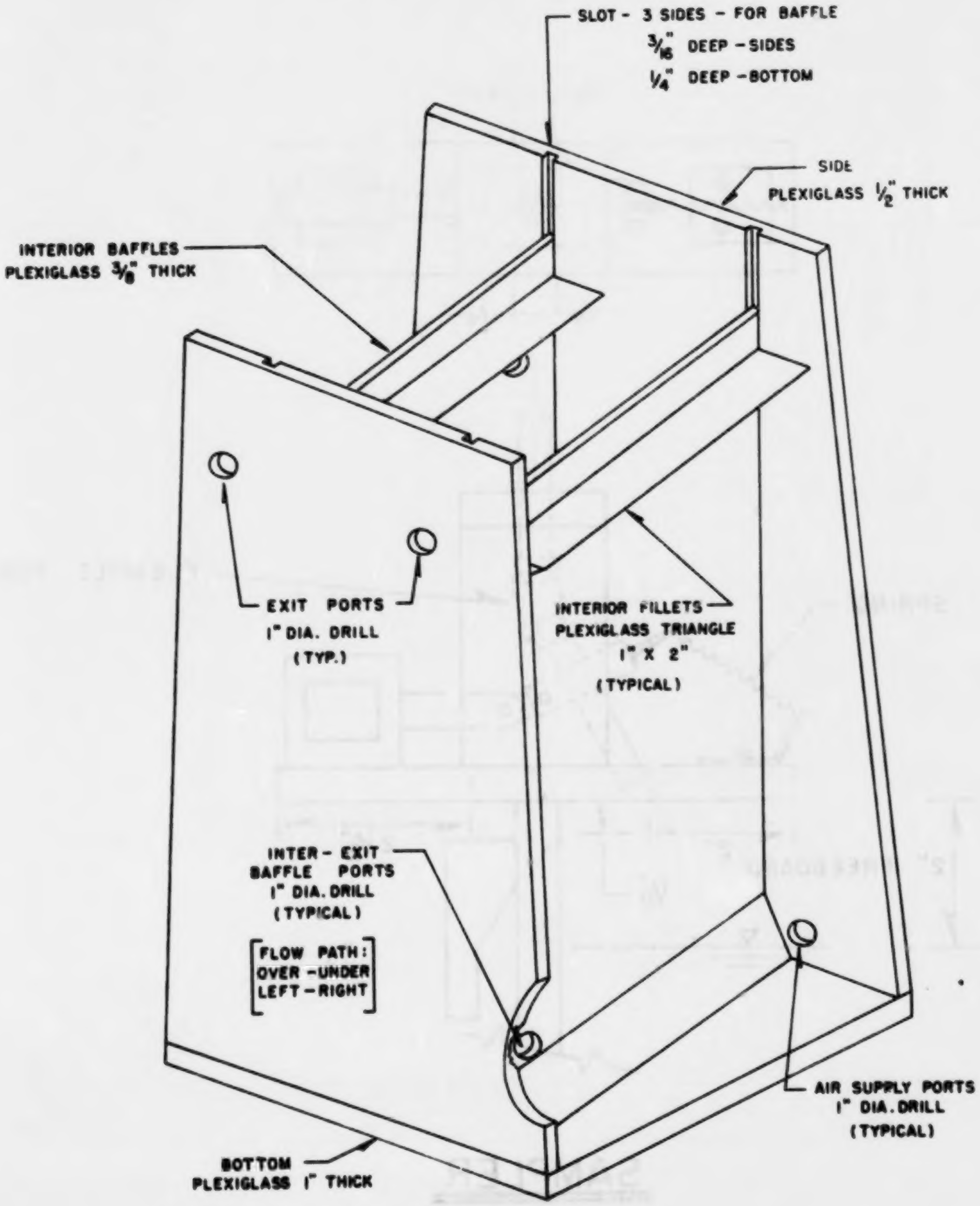
FIGURE 2


℄ AIR SUPPLY PORT
1 ½"
5"
3 ¼"
1 ½"
1 ½"
1 ½"
SLOTS FOR SAMPLERS
℄ EXIT PORT
℄ ¼" DIA. STAINLESS STEEL TIE BARS
12"
1 ½"
4"
21"
25"
℄ AIR SUPPLY PORT
1"
11"
12"
12"
1 ½"
1 ½"
2 ½"
7 ½"
℄ INTER -EXIT PORTS
2 ½"
47 ⅞"

AERATION TANK CONSTRUCTION

SCALE: 1" = 10"

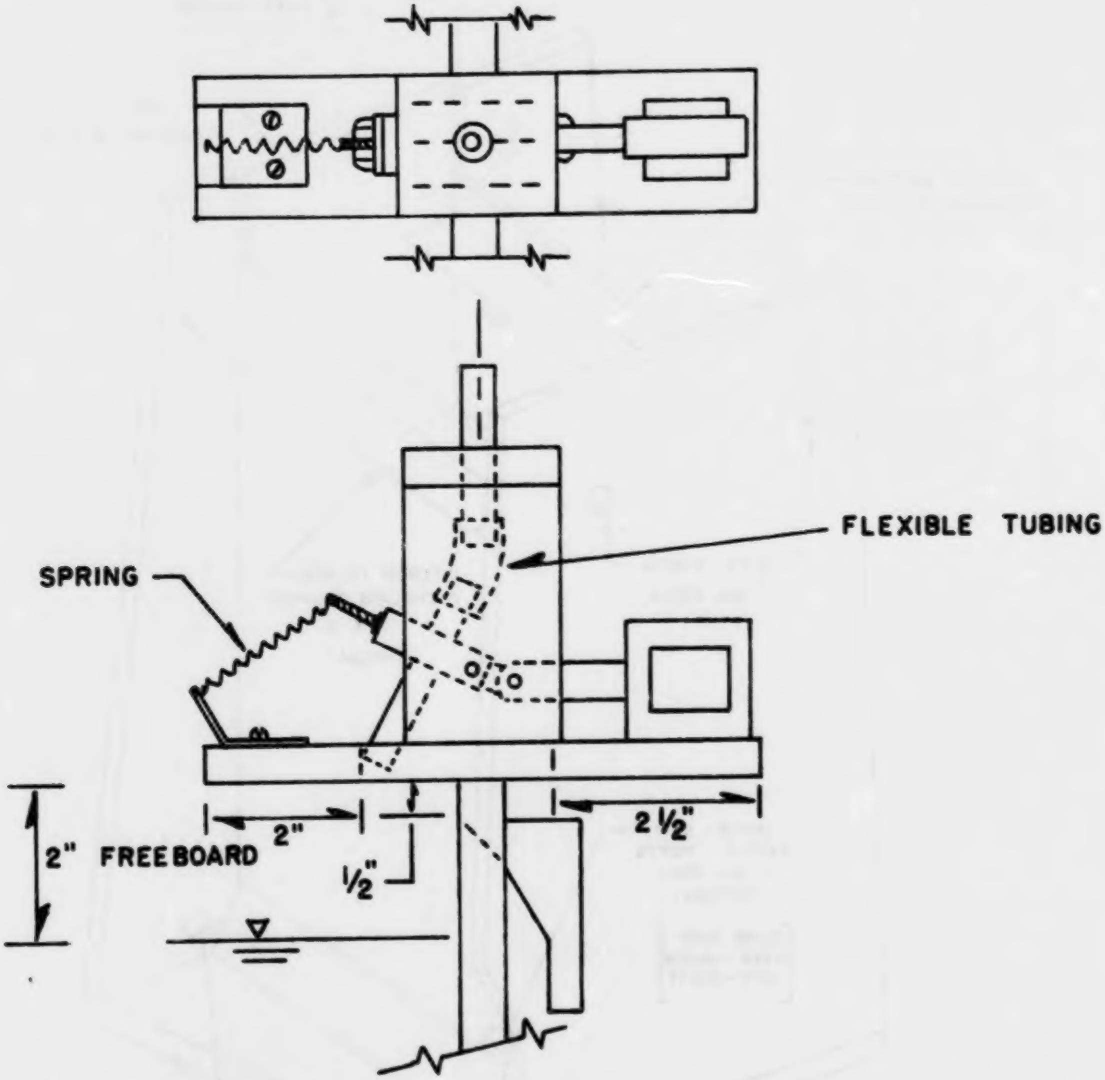
FIGURE 3


SLOT - 3 SIDES - FOR BAFFLE
3/16" DEEP - SIDES
1/4" DEEP - BOTTOM
SIDE
PLEXIGLASS 1/2" THICK
INTERIOR BAFFLES
PLEXIGLASS 3/8" THICK
EXIT PORTS
1" DIA. DRILL
(TYP.)
INTERIOR FILLETS
PLEXIGLASS TRIANGLE
1" X 2"
(TYPICAL)
INTER - EXIT
BAFFLE PORTS
1" DIA. DRILL
(TYPICAL)
FLOW PATH:
OVER - UNDER
LEFT - RIGHT
AIR SUPPLY PORTS
1" DIA. DRILL
(TYPICAL)
BOTTOM
PLEXIGLASS 1" THICK

AERATION TANK CHAMBER — DETAIL

SCALE : 1" = 5"

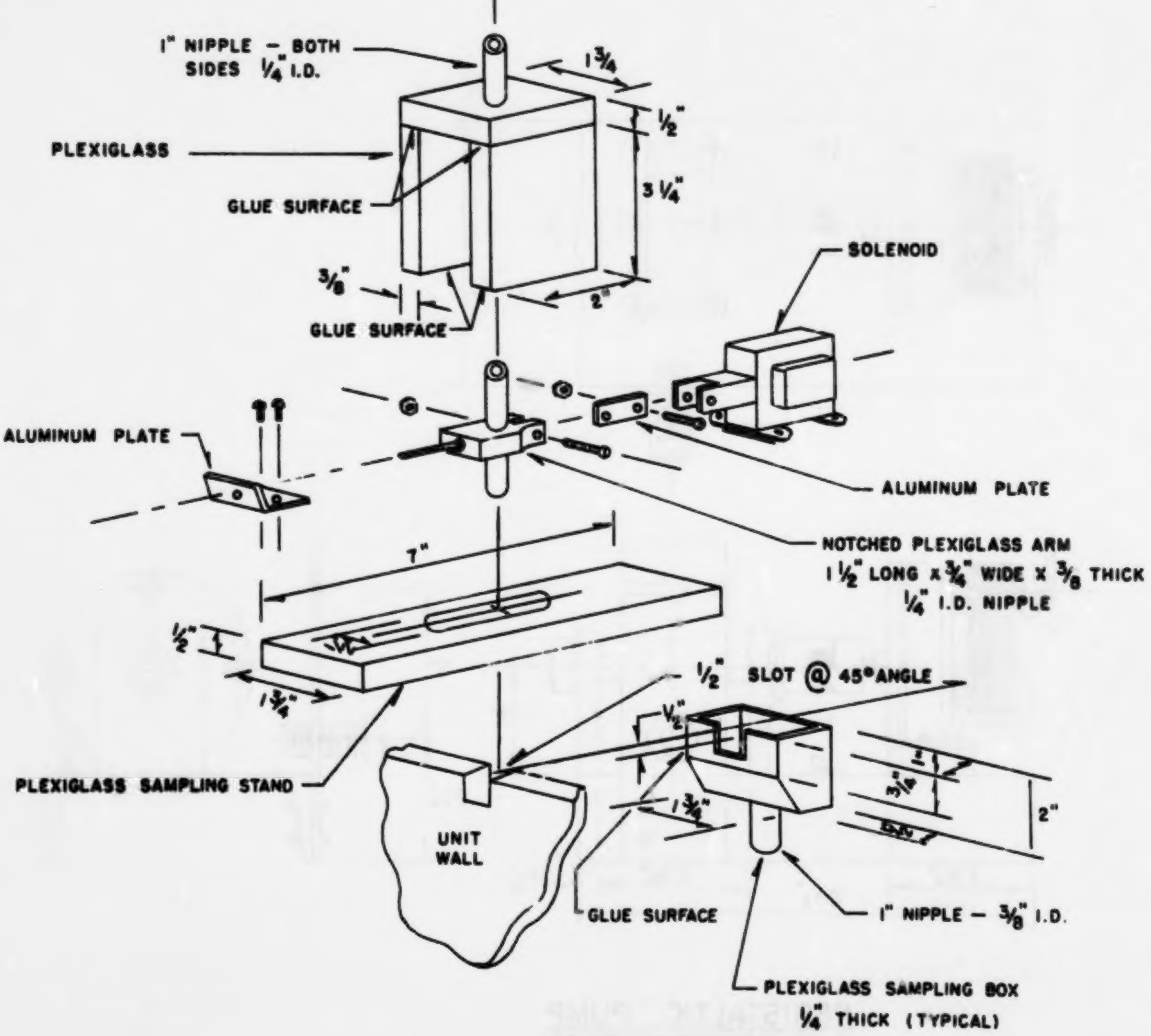
FIGURE 4


FLEXIBLE TUBING
SPRING
2" FREEBOARD
2"
1/2"
2 1/2"

SAMPLER

SCALE: 1" = 3"

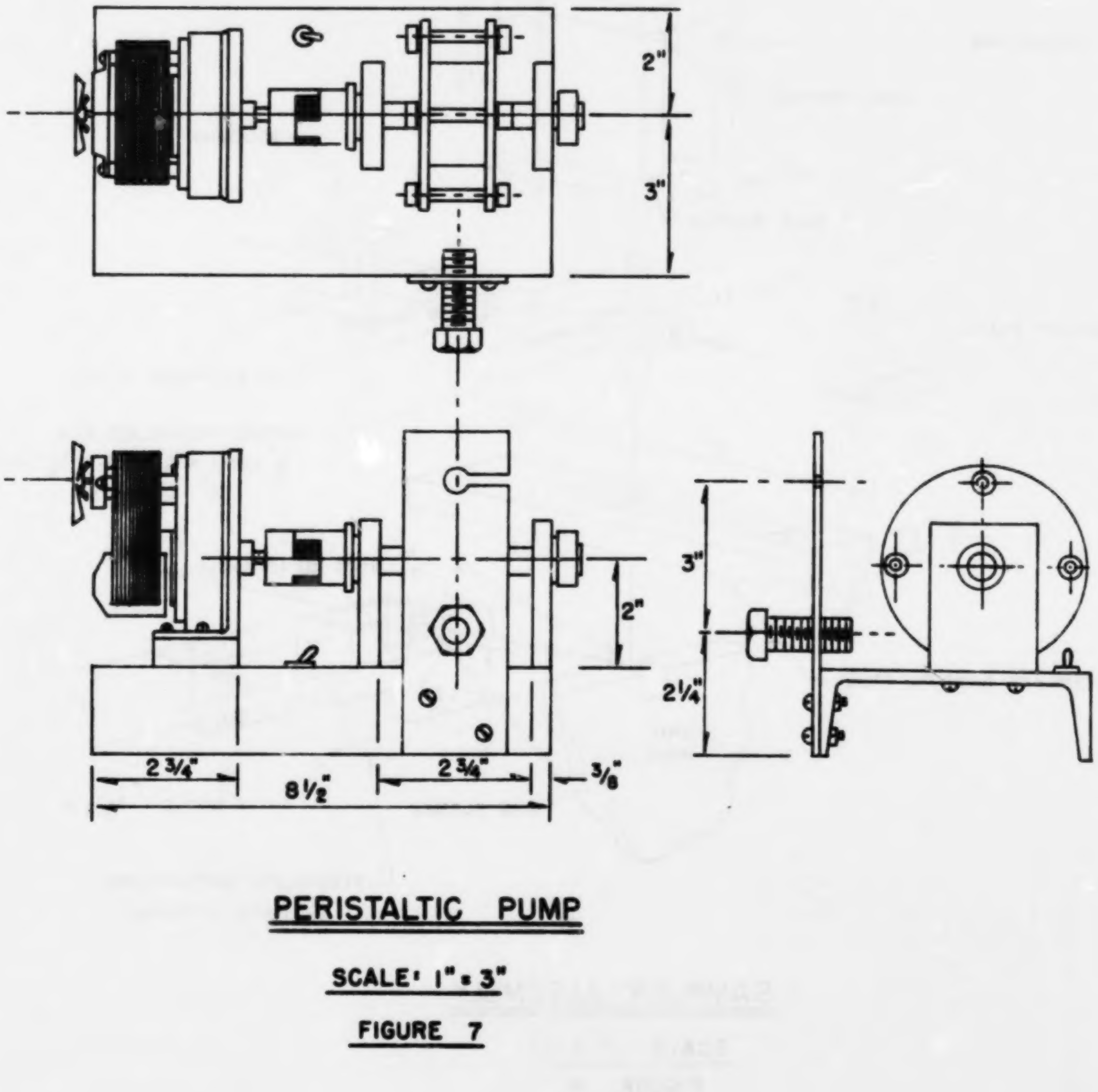
FIGURE 5


1" NIPPLE – BOTH SIDES 1/4" I.D.
1 3/4
1/2"
PLEXIGLASS
3 1/4"
GLUE SURFACE
3/8"
2"
GLUE SURFACE
SOLENOID
ALUMINUM PLATE
ALUMINUM PLATE
NOTCHED PLEXIGLASS ARM
1 1/2" LONG x 3/4" WIDE x 3/8 THICK
1/4" I.D. NIPPLE
7"
1/2"
1 3/4"
1/2" SLOT @ 45° ANGLE
1/2"
PLEXIGLASS SAMPLING STAND
UNIT WALL
1 3/4"
2"
GLUE SURFACE
1" NIPPLE – 3/8" I.D.
PLEXIGLASS SAMPLING BOX
1/4" THICK (TYPICAL)

SAMPLER ASSEMBLY

SCALE 1" = 3"

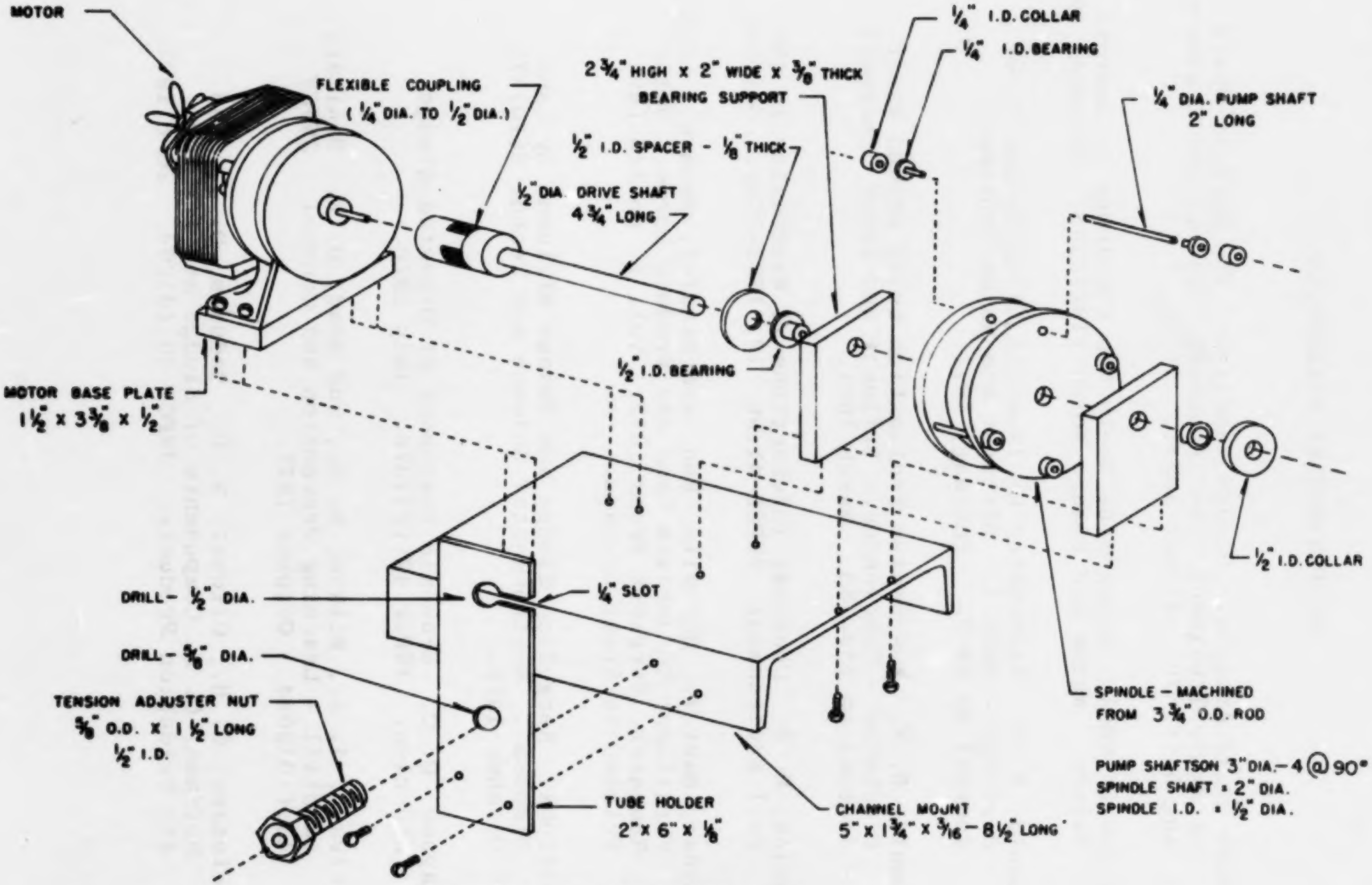
FIGURE 6


2"
3"
3"
2"
2 1/4"
2 3/4"
8 1/2"
2 3/4"
3/8"

PERISTALTIC PUMP

SCALE: 1" = 3"

FIGURE 7


MOTOR
FLEXIBLE COUPLING (1/4" DIA. TO 1/2" DIA.)
2 3/4" HIGH x 2" WIDE x 3/8" THICK BEARING SUPPORT
1/4" I.D. COLLAR
1/4" I.D. BEARING
1/4" DIA. PUMP SHAFT 2" LONG
1/2" I.D. SPACER - 1/8" THICK
1/2" DIA. DRIVE SHAFT 4 3/4" LONG
1/2" I.D. BEARING
MOTOR BASE PLATE 1 1/2" x 3 3/8" x 1/2"
1/2" I.D. COLLAR
DRILL- 1/2" DIA.
1/4" SLOT
DRILL- 5/8" DIA.
TENSION ADJUSTER NUT 5/8" O.D. x 1 1/2" LONG 1/2" I.D.
SPINDLE - MACHINED FROM 3 3/4" O.D. ROD
PUMP SHAFTSON 3" DIA.- 4 @ 90°
SPINDLE SHAFT = 2" DIA.
SPINDLE I.D. = 1/2" DIA.
TUBE HOLDER 2" x 6" x 1/8"
CHANNEL MOUNT 5" x 1 3/4" x 3/16 - 8 1/2" LONG

PERISTALTIC PUMP ASSEMBLY

SCALE: 1" = 3"

FIGURE 8

SUPPLEMENTARY REFERENCES

1 Anon Staff Article. Sludge Handling: The Hardest Phase of Waste Treatment. Environmental Science and Engineering 5:(8)670. August 1971.

2 Focus on OSHA. Management Meets New Challenge to Improve Safety. Water and Sewage Works 119(10)58. November 1972.

3 Gould, B. W. Wastewater Reclamation Using Ground Water Recharge - Part 1. Effluent and Water Treatment Journal pp 88-95. February 1971.

4 Gould, B. W. Wastewater Reclamation Using Ground Water Discharge - Conclusion. Effluent and Water Treatment Journal pp 139-143. March 1971.

5 Hajek, B. F. Chemical Interactions of Wastewater in the Soil Environment. JWPCF 41:No. 10, 1775-1786. October 1969.

6 Lynam, Bart T., Sosewitz, Ben, and Hinsley, Thomas. Liquid Fertilizer to Reclaim Land and Produce Corps. Water Research, Pergamon Press 1972. Vol. 6, pp 545-549. Printed in Great Britain.

7 Outlook. Recycling Sludge and Sewage Effluent by Land Disposal. Environmental Science and Techn. 6(10)871. October 1972.

8 Raynes, B. C. Economic Transport of Digested Sludge Slurries. JWPCF 42:(7)1379. July 1970.

9 Salvato, J. A., Wilkie, W. G., and Mead, B. E. Sanitary Landfill - Leaching Prevention and Control. JWPCF 43:(10)2084. October 1971.

10 Teletzke, G. H., Gitchel, W. B., Deddams, D. J., and Hoffman, C. A. Components of Sludge and Its Wet Air Oxidation Products. JWPCF 39:(9)994. June 1967.

23-22

BENCH DATA ACTIVATED SLUDGE

I GENERAL

A Flow through units

Nominal Capacity: Aerator 4.8 liters
Settler 0.7 liter

B Fed on a semi-continuous basis

1 Hydraulic loading: 18-19 liters per day

2 Approximately 75% of the feed volume added from 10 a.m. to 4 p.m. daily. Remainder at a lower rate, 7 days/week.

C Solids or liquid remaining on the following morning were added as a slug dose as rapidly as possible using added settler capacity, if needed, for return of solids washed out.

D Effluent analysis on daily composites preserved with $HgCl_2$.

1 Resp. tests on ML before and after feeding the same feed and proportions as in the test unit by DO probe technique. Monday, Wednesday and Friday.

2 MLSS and Settleability samples taken just before starting the daily feed.

3 ML Oil taken on catch samples. Calculated on dry solids basis. Effluent oil - (SS < 10 mg/liter) 2 - 4 mg/liter on Unit 1; 3-7 mg/liter on Unit 2.

II FEED CHARACTERISTICS

A Weekly average - No. 1 Unit

1	Mineral Oil	180 mg/day	10 mg/liter
2	Phenol	1000 mg/day	56 mg/liter
3	Fish Meal	2500 mg/day	140 mg/liter

System Nitrogen deficiencies of a borderline nature stabilized by 5 mg/liter NH_3 - N as NH_4Cl added after 10th day on No. 2 unit.

Tap water diluent used.

B Oxygen demand (COD basis) 5200 mg/day (average). 290 mg COD/liter average (No. 1).

C No. 2 Unit received two times the organic load of No. 1 Unit.

D Organic feed for each unit, each day, programmed according to the weekly organic load fluctuation of a sample municipal operation as follows:

Sunday	0.4 × weekly average
Monday	1.2 × weekly average
Tuesday	1.4 × weekly average
Wednesday	0.9 × weekly average
Thursday	1.1 × weekly average
Friday	1.5 × weekly average
Saturday	0.5 × weekly average

ACKNOWLEDGMENT

These data were collected on Bench Unit operations and analyses collected as a cooperative venture of the entire Training Group, F.P. Nixon, Coordinator, October and November 1966.

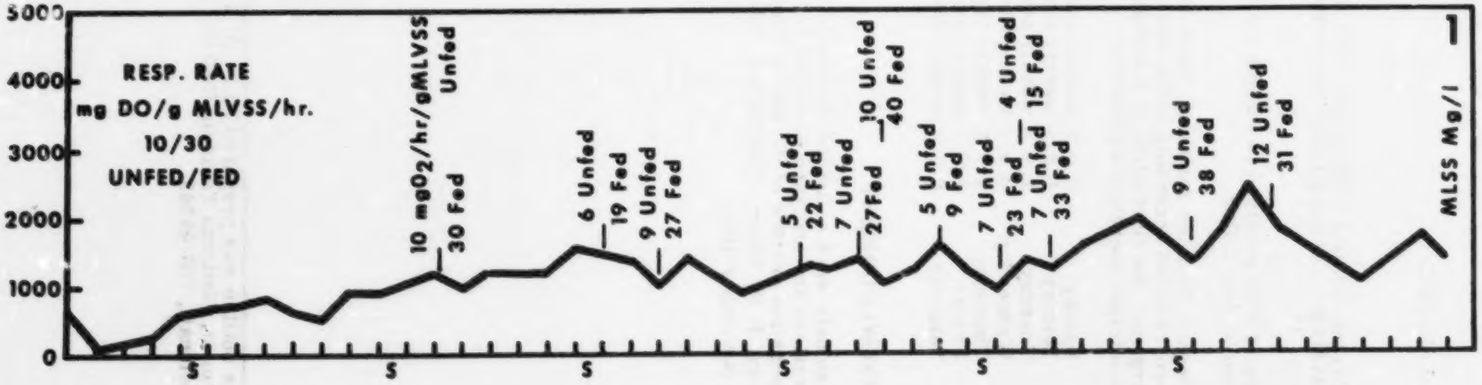
This outline was prepared by F. J. Ludzack, Chemist, National Training Center, OWP, EPA, Cincinnati, OH 45268.

24.2

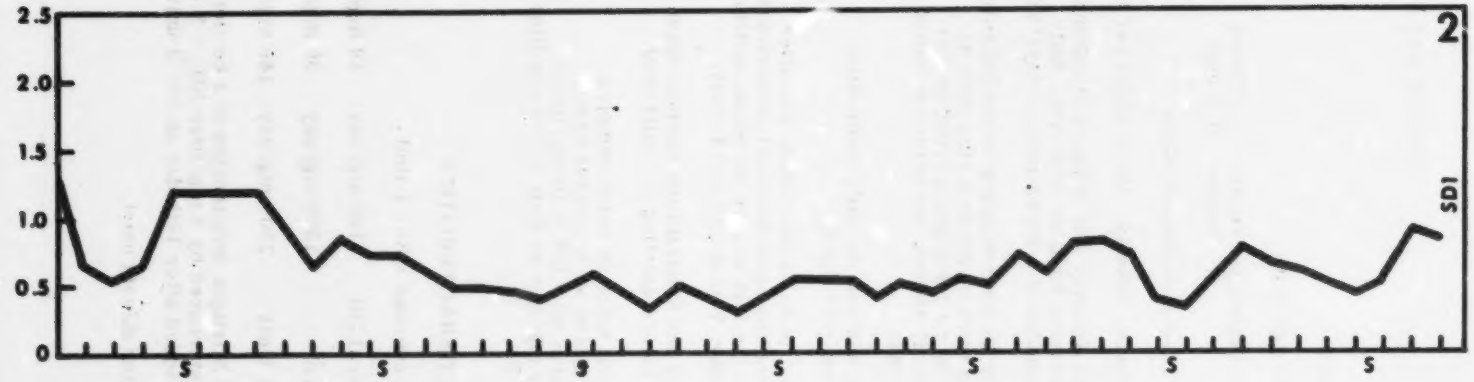
Unit No. 1-1

Figure 1

mg MLSS/liter in Aerator



Sludge Density Index - SDI

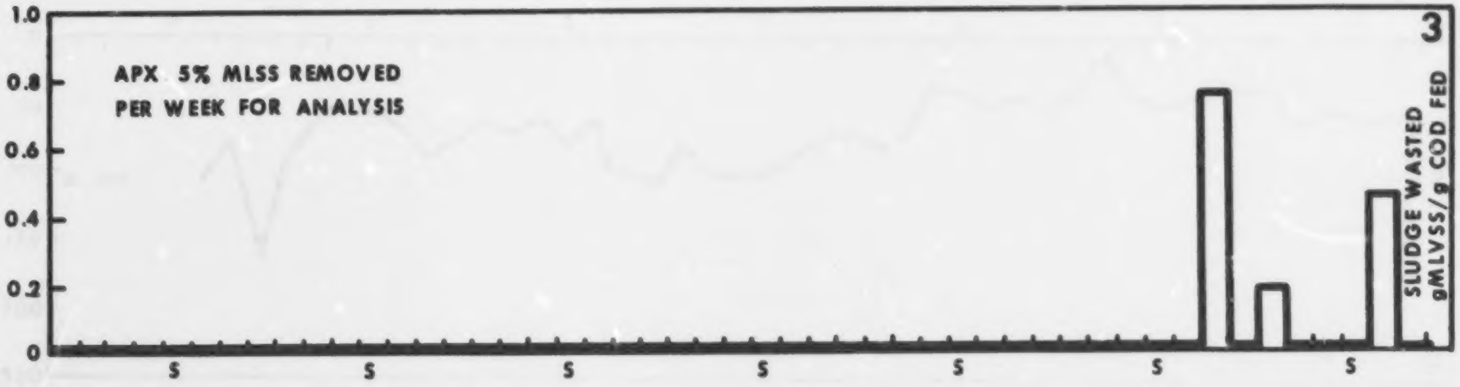


Days of the Week - Sundays Indexed

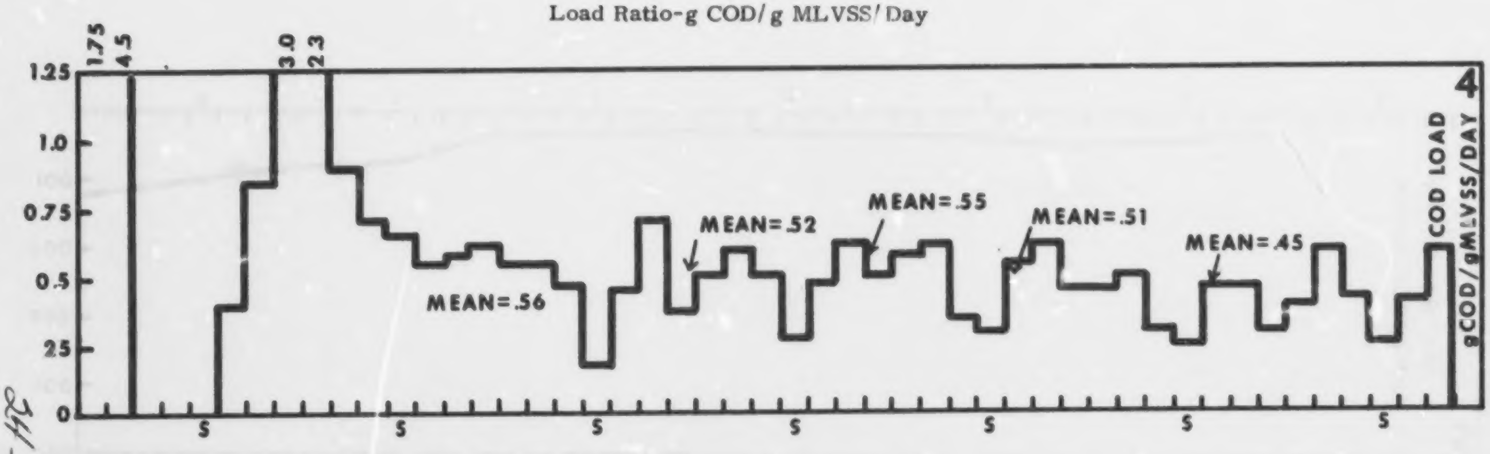
Figure 2

Unit No. 1-2

Wasted Excess Solids



Load Ratio-g COD/ g MLVSS/ Day



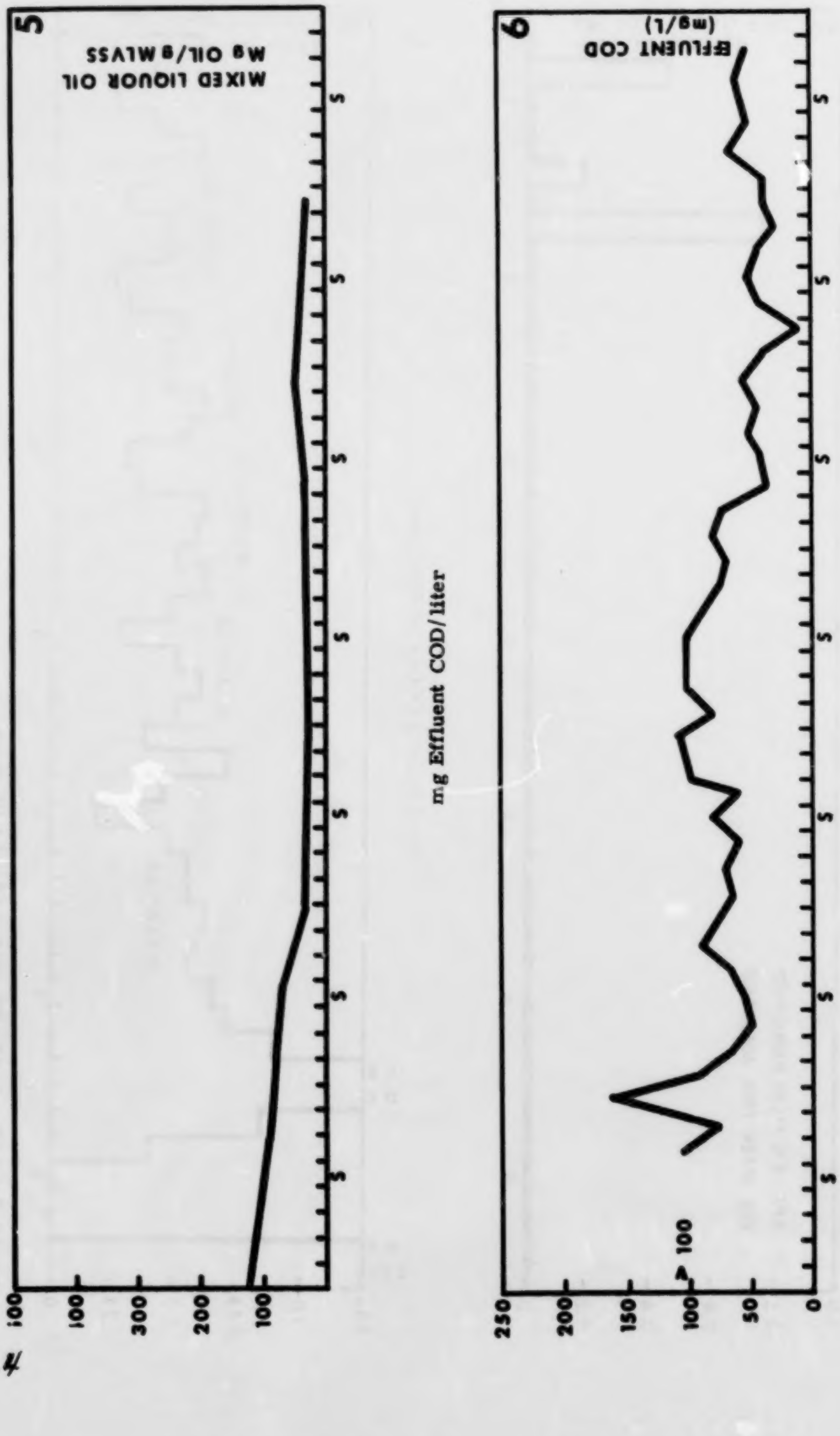
BASED ON 90% VOLATILITY AND MEAN 24-HR MLSS

Day of the Week - Sundays Indexed

Unit No. 1-3

Figure 3

mg Oil/g MLVSS

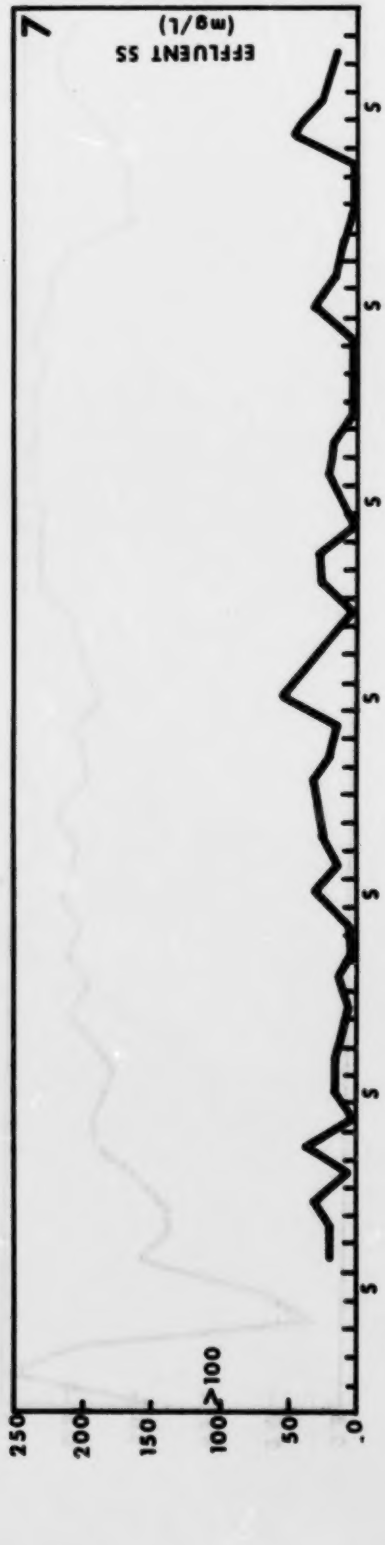


Day of the Week - Sundays Indexed

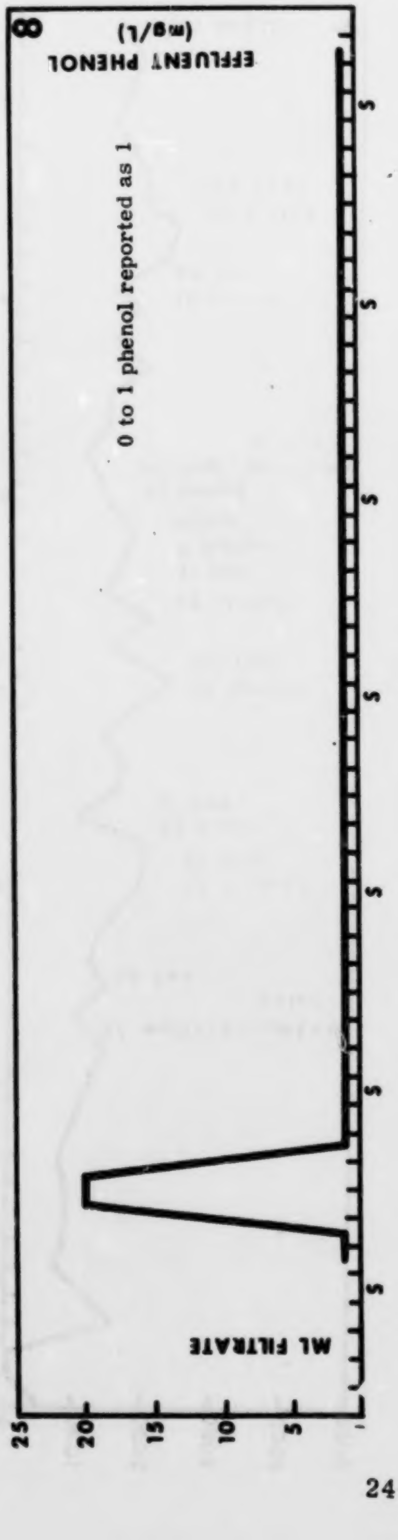
Unit No. 1-4

Figure 4

Effluent, mg SS/liter



Effluent, mg Phenolics/liter

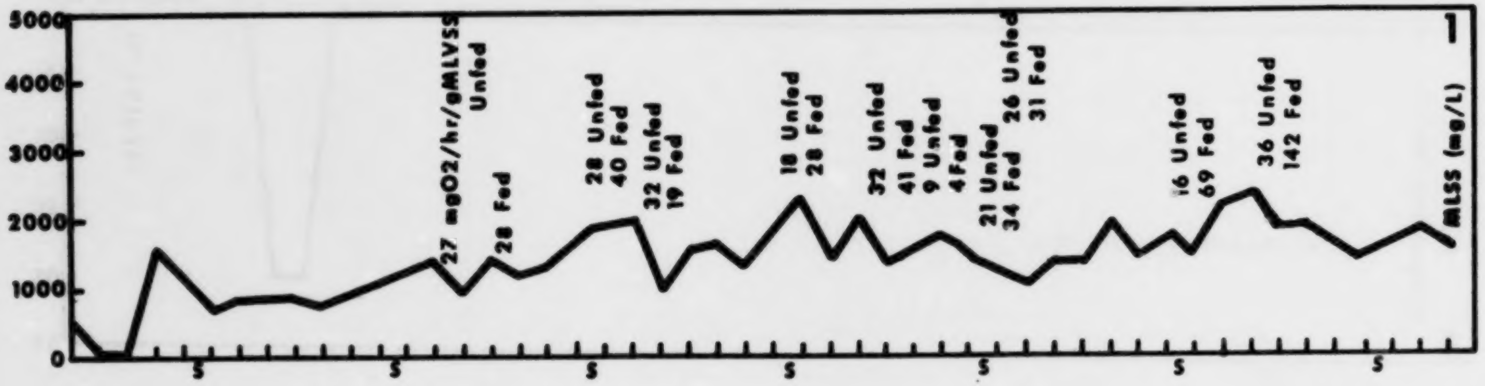


Days of the Week - Sundays Indexed

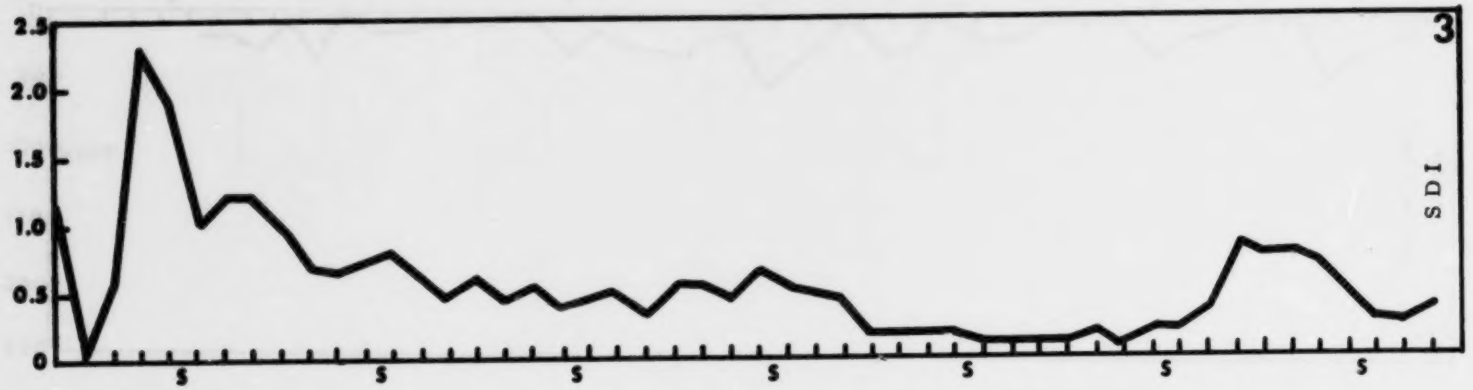
Figure 5

Unit No. 2-1

mg MLSS/liter



Sludge Density Index - SDI

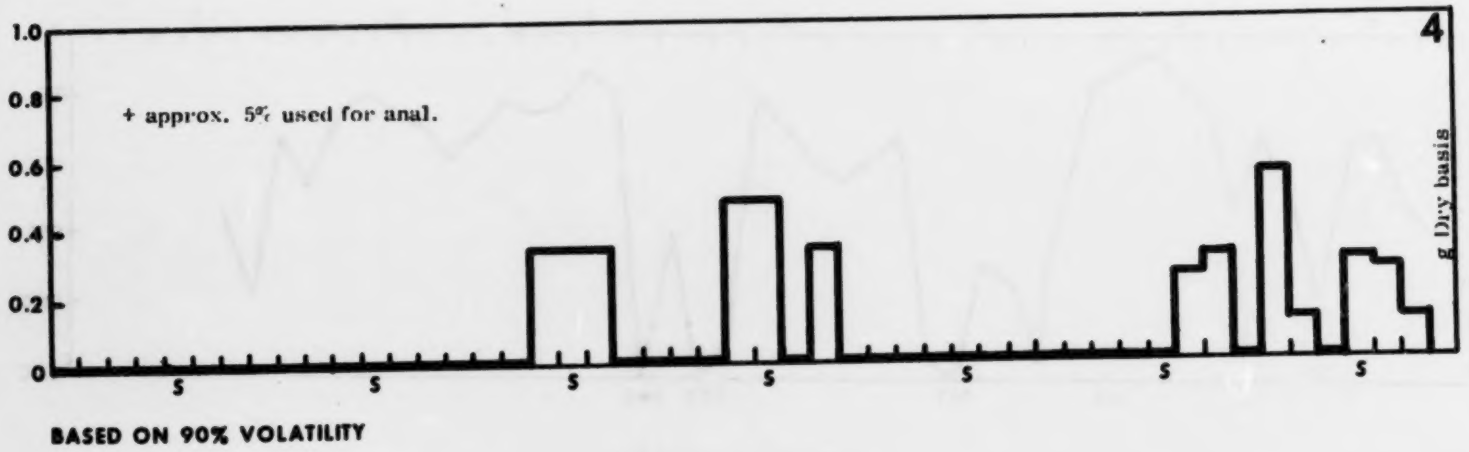


Days of the Week - Sundays Indexed

Figure 6

Unit No. 2-2

Wasted Excess Solids



Load Ratio - g COD/ g MLVSS/ Day

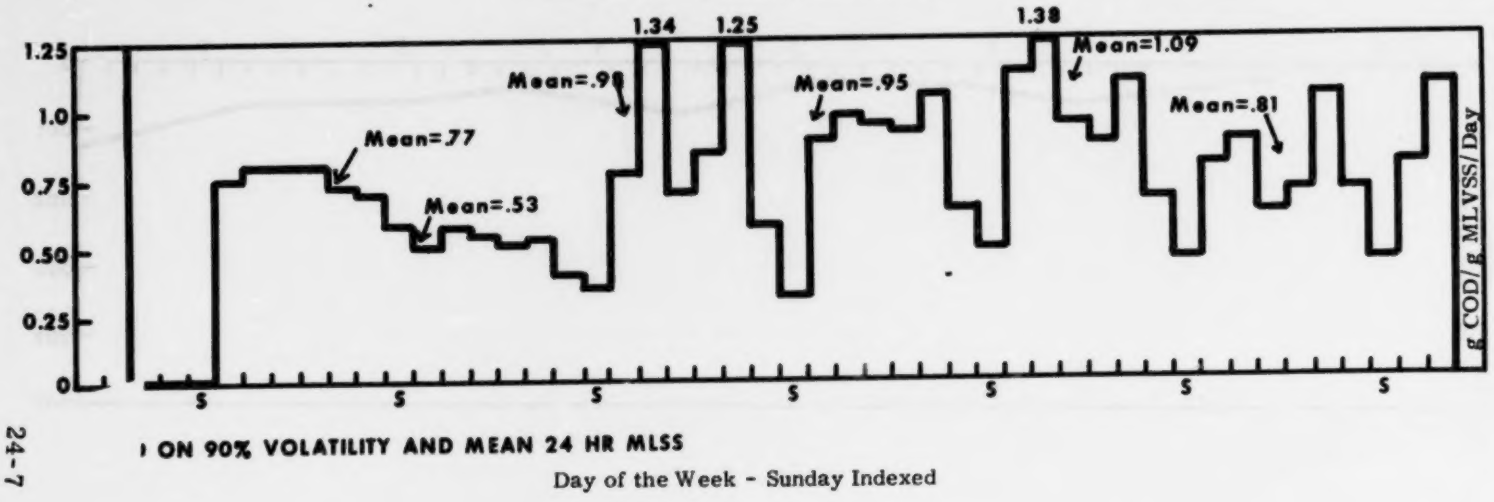
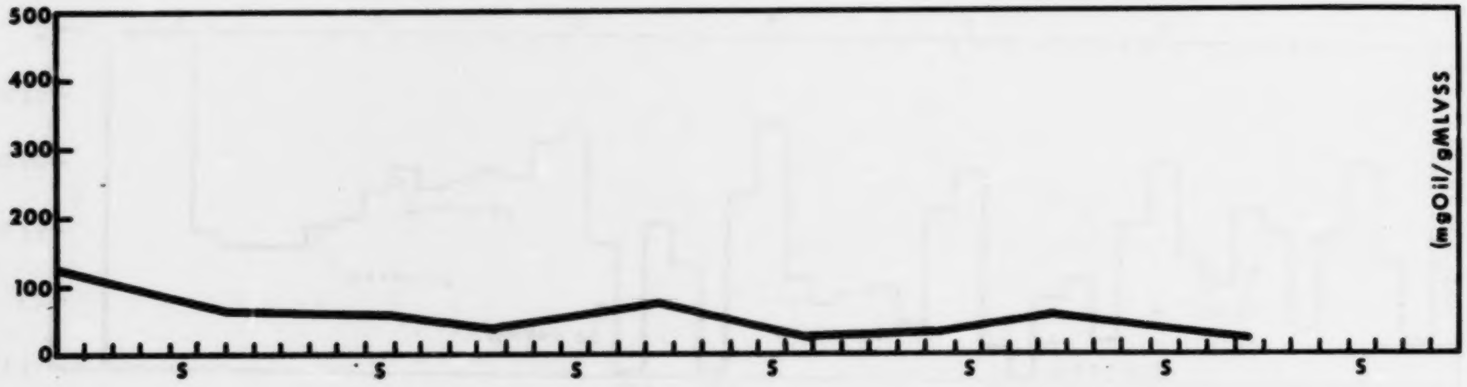


Figure 7

Unit No. 2-3

mg Oil/ g MLVSS



mg Effluent COD/ liter

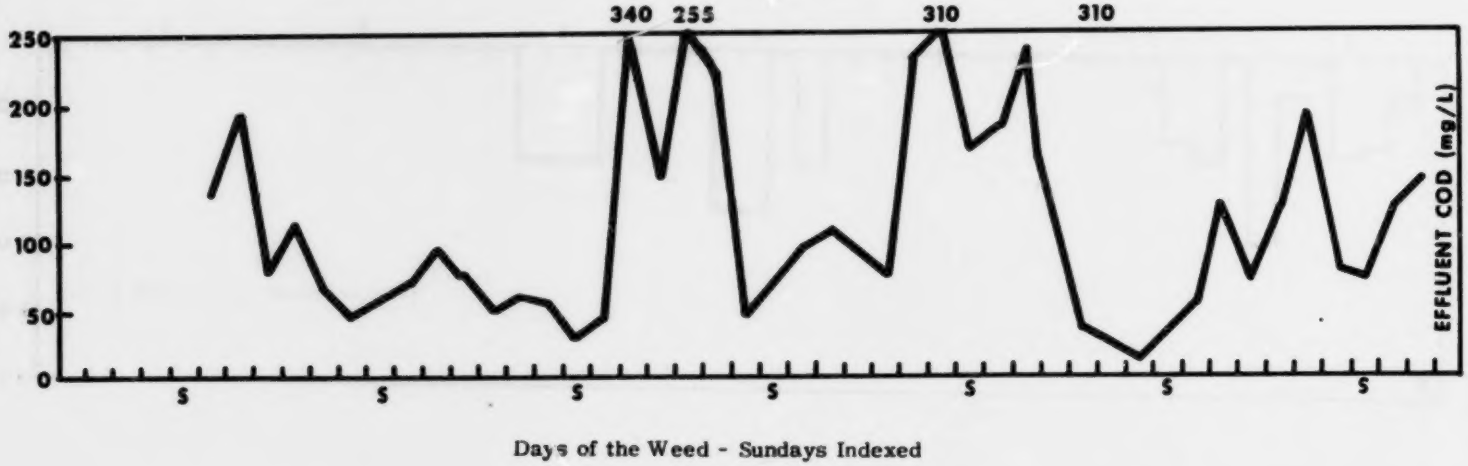
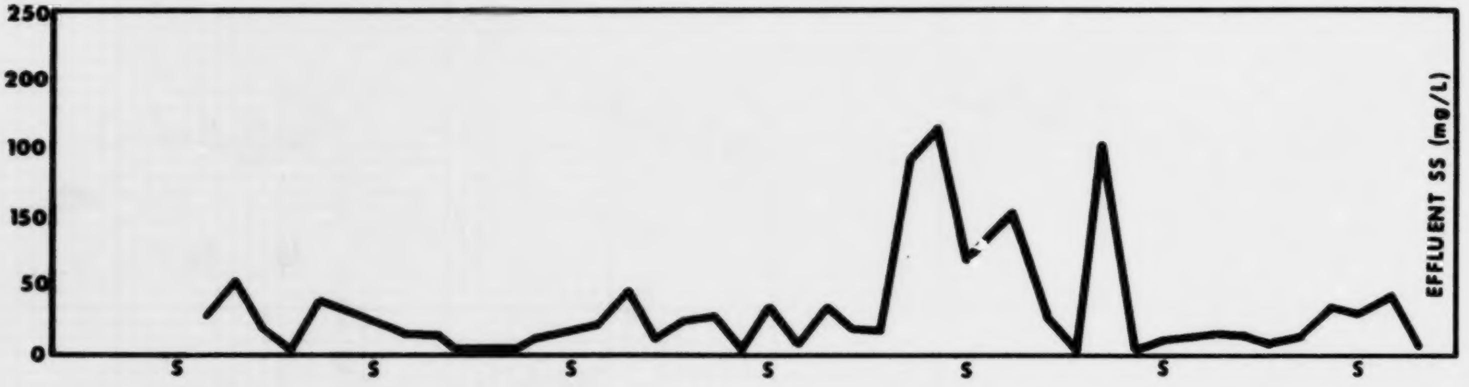


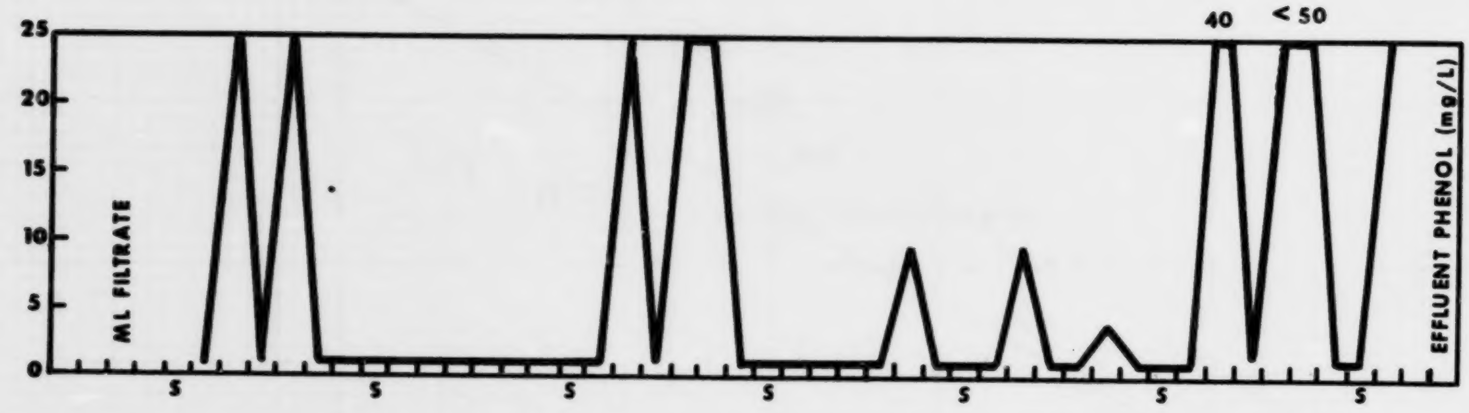
Figure 8

Unit No. 2-4

Effluent / mg SS/liter



Effluent Phenolics mg/liter

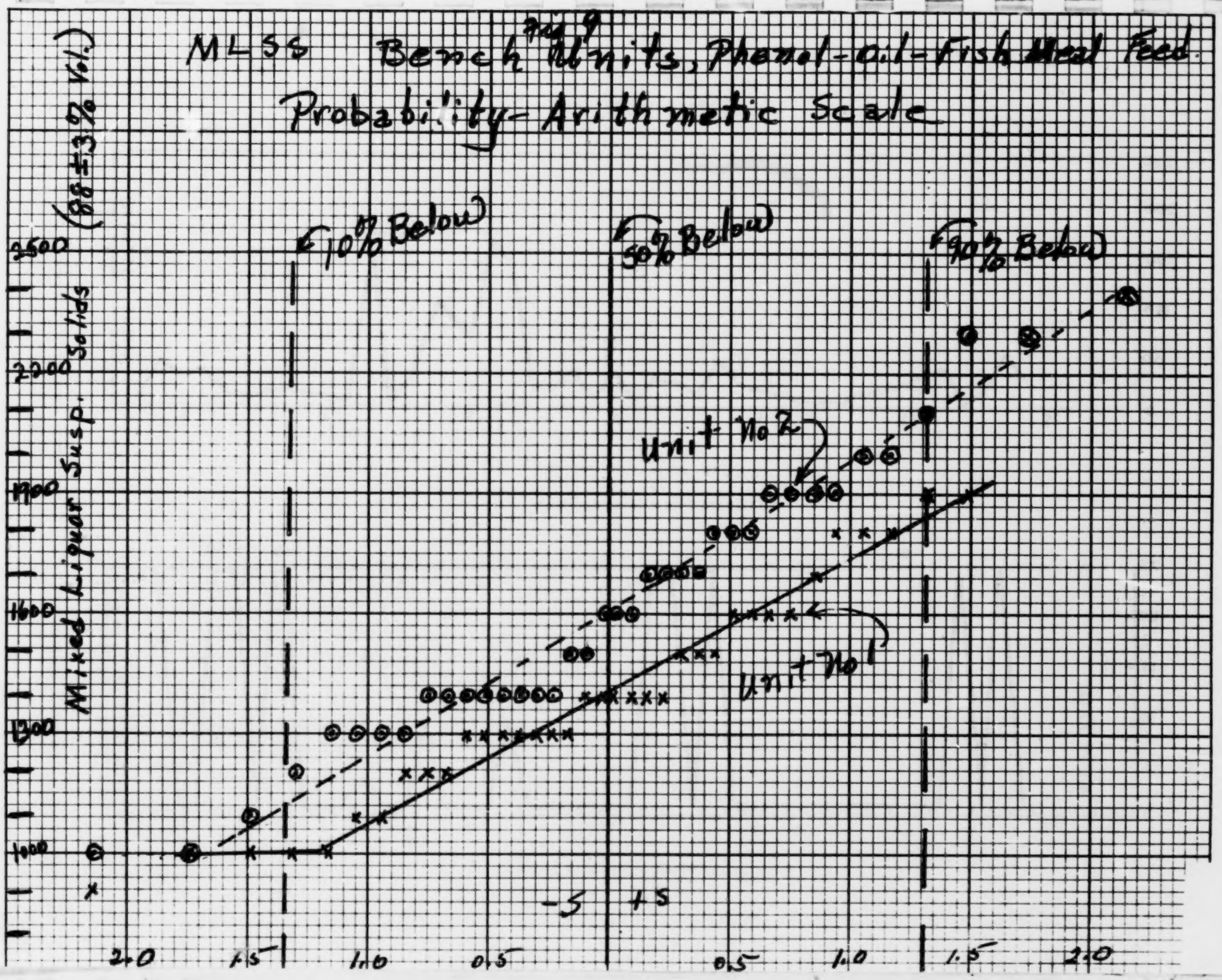


Days of the Week - Sundays Indexed

Fig 9

MLSS Bench Units, Phenol-Oil-Fish Meal Feed

Probability-Arithmetic Scale



24-10

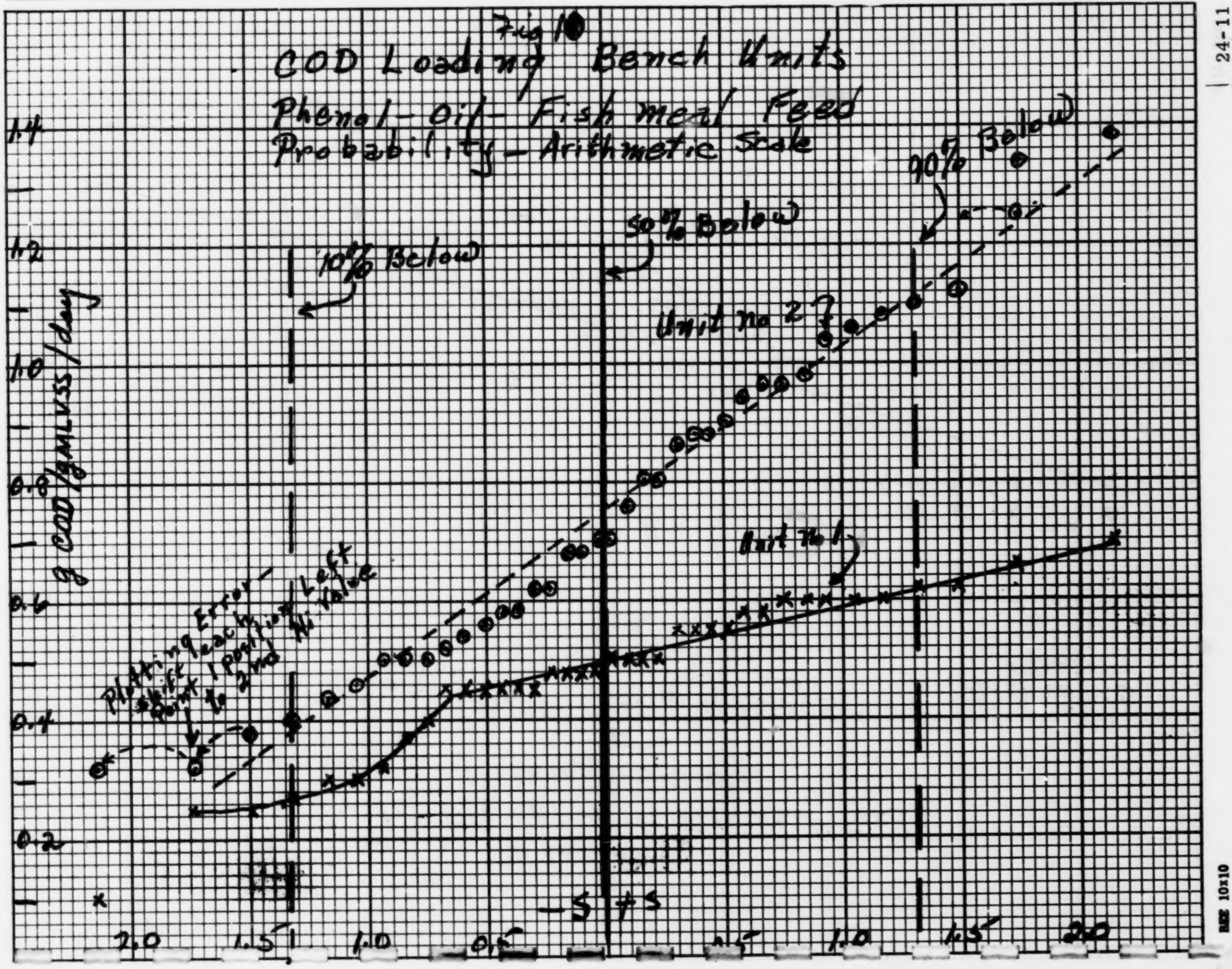


Fig 10

COD Loading Bench Units

Phenol - Oil - Fish meal Feed

Probability - Arithmetic Scale

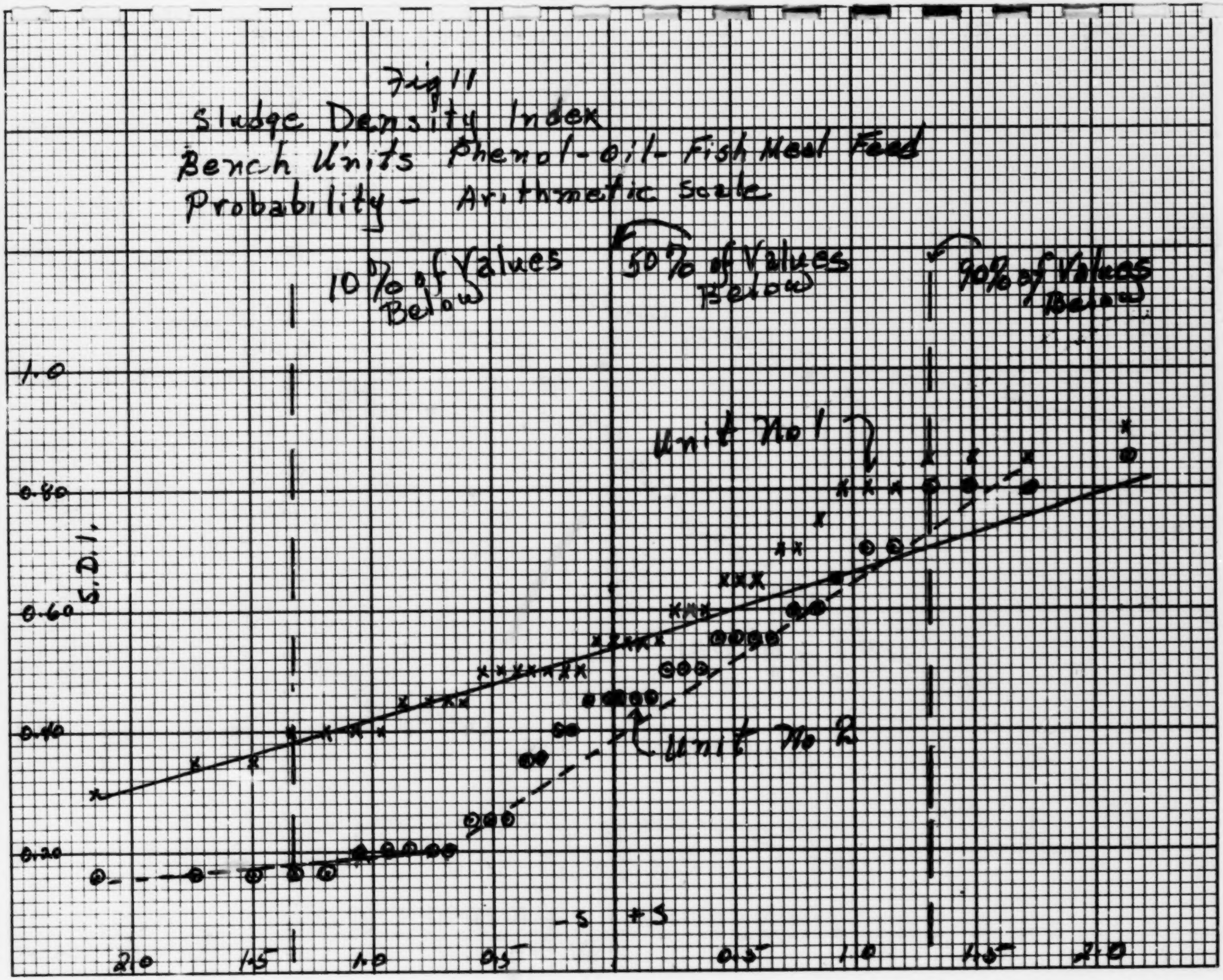


Fig 11

Sludge Density Index
Bench Units Phenol-oil-Fish Meal Feed
Probability - Arithmetic Scale

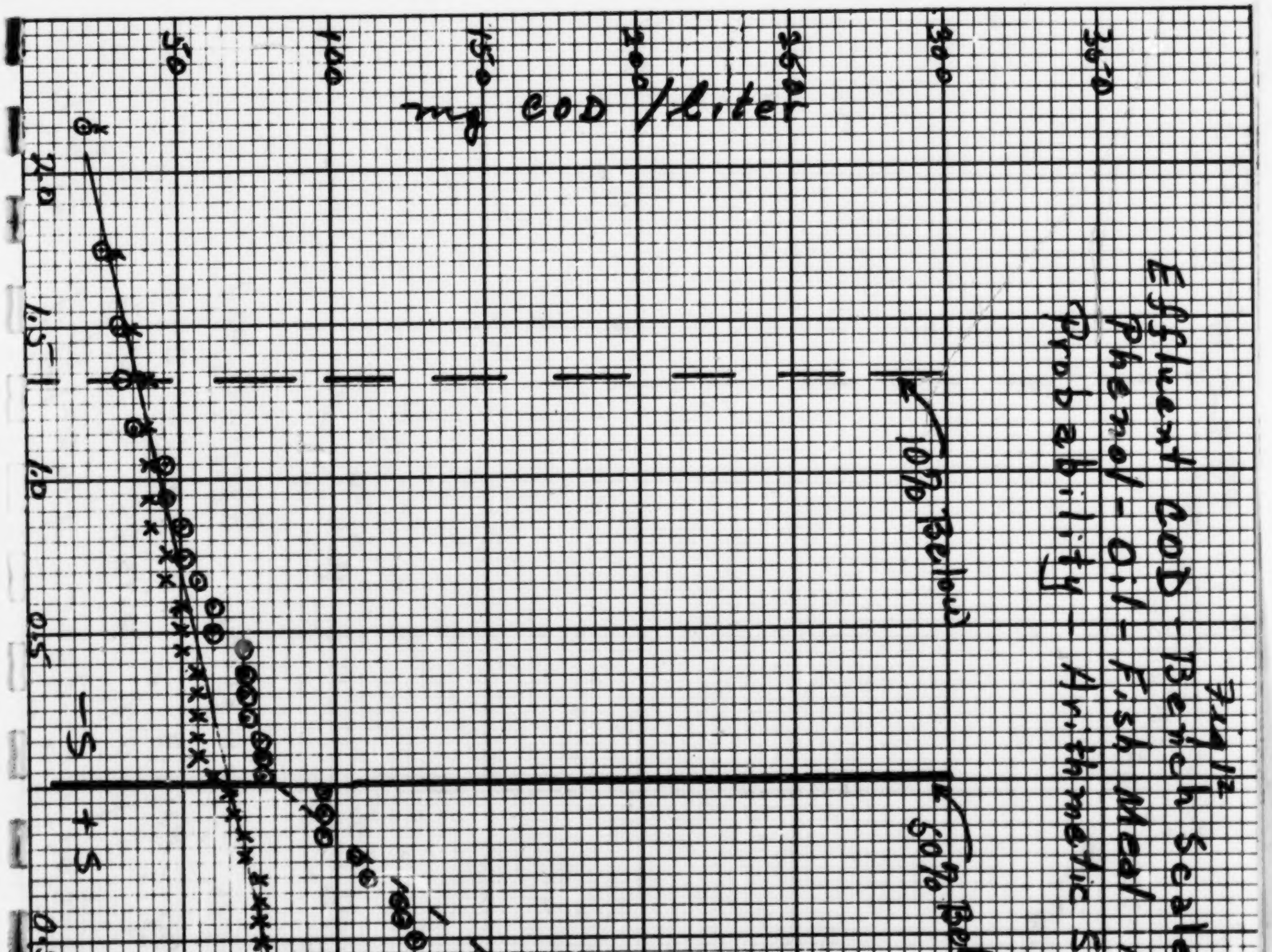


Fig 12
Effluent COD - Bench Scale Units, (Cl⁻ Corr. 2 hr Reflux)
Phenol - Oil - Fish Meal Feed
Probability - Arithmetic Scale

BEE 10x10

24-13

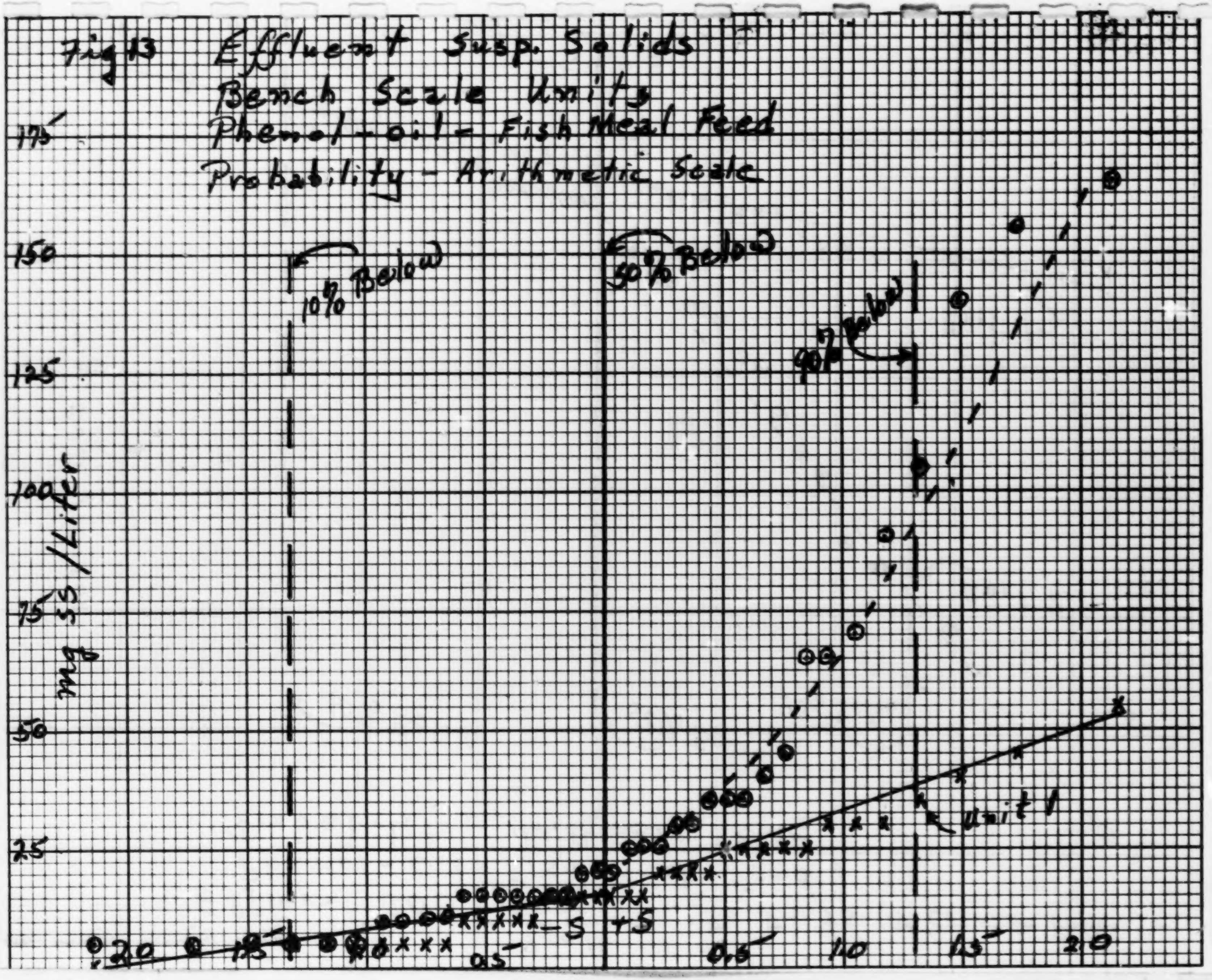


Fig 13 Effluent Susp. Solids
Bench Scale Units
Phenol-oil-Fish Meal Feed
Probability-Arithmetic Scale

BEE 10x10
24-14

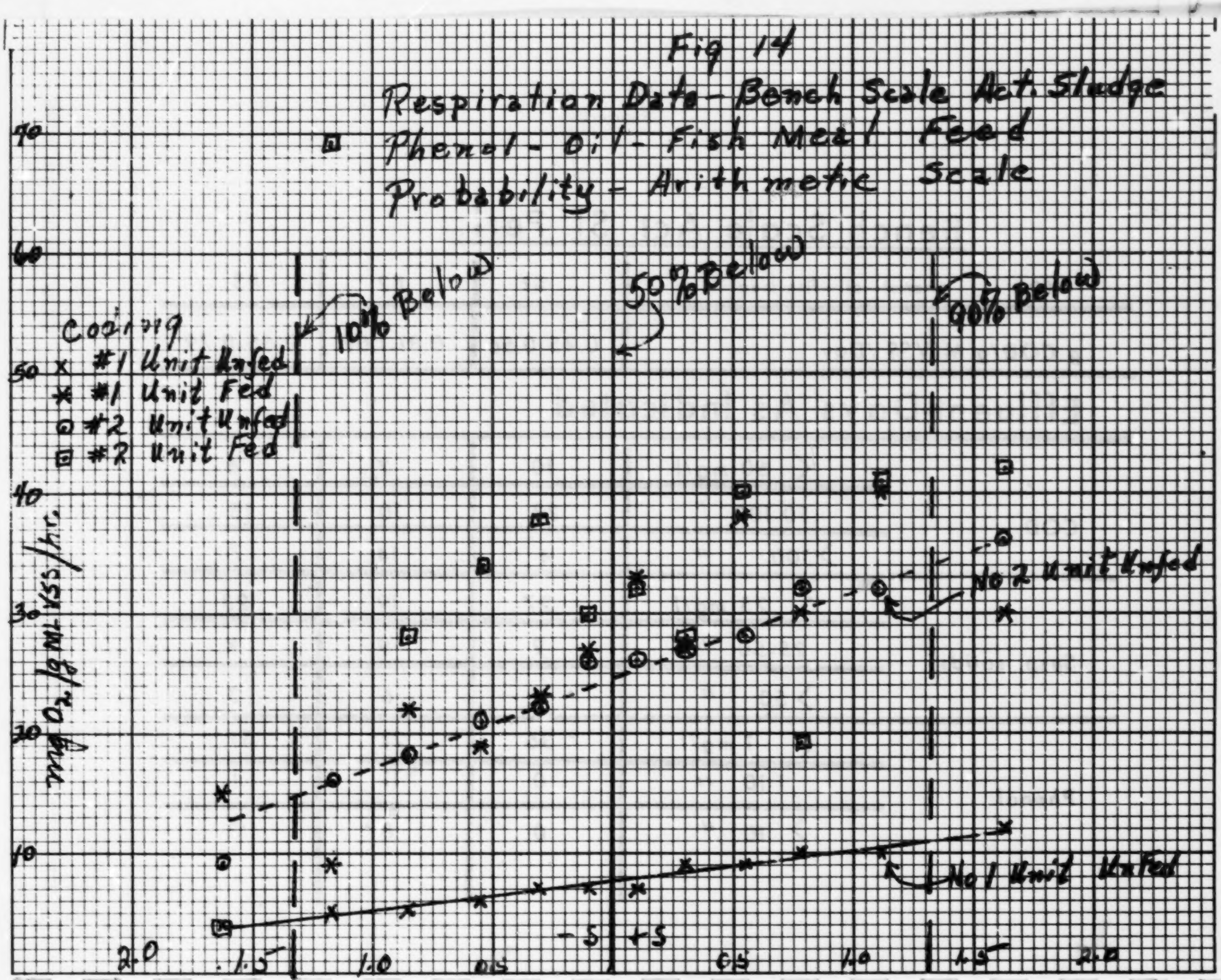


Fig 14

Respiration Data - Bench Scale Act. Sludge
Phenol - Oil - Fish Meal Feed
Probability - Arithmetic Scale

24-15
BEE 10x10

Figure 15

Bench Scale Act. Sl. Perf.

FEED: phenol—oil—fish meal		#1	#2	#3
g COD/g MLVSS /Day		0.45-0.56	0.81-1.09	0.65-0.79
Effluent-Days As Indicated				
COD	< 50 mg/l	10	7	8
	50-100 "	23	10	18
	> 100 "	4	14	7
Susp. solids	< 25 mg/l	27	19	23
	25-50 "	9	9	8
	> 50 "	1	6	3
Phenol	< 1 mg/l	36	21	31
	1-10 "	0	11	1
	> 10 "	0	8	2

STATUS OF ACTIVATED SLUDGE PROCESS

I CURRENT STRESS

A Increasing emphasis on secondary treatment and up-grading effluent quality has resulted in many new plants, additions to existing plants and conversion of other processes to activated sludge.

B There has been a long history of operational problems connected with the activated sludge process.

1 Design often stressed tankage and economy rather than performance of a dynamic biological system. Versatility and workability during operation often were reduced by inadequate understanding of process and operational realities or subsequent "cuts" in proposed facilities.

2 The lack of knowledge of operating personnel in energy and growth characteristics and operating control techniques often results in low grade effluent quality. Public apathy, inadequate operational budgets for manpower, materials, and maintenance often relegate the facility to a "monument" status instead of a functional entity.

C Population density and activity changes have forced a reevaluation of the "known". Design changes necessarily must follow to up-grade environmental quality.

D Many alternates are available for the activated sludge process. The versatility of the process and possibilities for supplementation for effluent quality improvement with respect to general or specific components cause it to be ranked very high among these alternates. The process is not dead yet; many of its potentials are not generally recognized.

II THEORY OF ACTIVATED SLUDGE

A The process was first reported in 1914 by Ardern & Lockett (1).

B Chemical vs biological theories caused much discussion.

1 Butterfield in 1935 (2) isolated Z. ramigera from activated sludge and developed pure culture activated sludge from Z. ramigera (3).

2 McKinney isolated several floc forming bacteria in 1950 and demonstrated that flocculation was associated with the stage of development (4).

C Energy concept for bacterial flocculation.

1 Work at the Massachusetts Institute of Technology (MIT) in 1951 developed relationships between food (energy) levels, growth and flocculation (4).

2 During a situation involving high food concentrations (energy), cell growth was rapid but flocculation was nil.

3 After available food had been metabolized into a lower free energy situation, flocculation occurred.

4 Protozoa assisted clarification.

D Recent research

1 The Z. ramigera concept has been supported.

2 The accumulation of poly beta hydroxybutyric acid (PHB) in the cell has been associated with flocculation.

3 Flocculation has been observed without PHB formation. Naturally occurring polyelectrolytes and other factors are associated.

E Basic Concepts

1 Bacteria metabolise organics with synthesis of new cells.

a Simple, soluble organics are metabolized first.

b Colloidal and suspended organics metabolized more slowly.

c A portion of the organics are oxidized to yield energy for synthesis.

d There is no metabolism without synthesis.

e A definite quantitative relationship exists between energy and synthesis.

2 At low energy levels, agitation promotes floc formation.

3 Endogenous metabolism of cell mass and storage products provides energy for regrowth and oxidation thus decreasing sludge mass.

4 Protozoa feed on bacteria and further reduce sludge mass; also improves clarification by pickup of scattered residues.

5 Overall reaction is synthesis followed by endogenous respiration.

6 All biochemical reactions are both quantitative and reproducible.

III MATHEMATICAL CONCEPTS AND DESIGN

A In the 1950's, efforts were directed toward mathematical design concepts (5).

B Eckenfelder's Equations

1 Initially developed in 1954

a BOD loading factor = $\frac{\text{lbs BOD/day}}{\text{lbs MLSS}}$

where: BOD = $\text{BOD}_{5\text{ day}}$

MLSS = mixed liquor suspended solids in process.

For calculation (90% removal)

= BOD_5 x 1.5 taken for La

$$= \frac{24\ \text{La}}{\text{Sa}\ t\ (1 + r)}$$

where: La = influent BOD-Average 24 hrs/day

Sa = average MLSS

t = aeration time (hrs) based on (Q + R) = (1 + r)

r = sludge recycle ratio

Q = inflow volume

R = recycle volume

b Lbs O_2/day = aLr + bMLVSS

where: a = 0.5 = lbs MLVSS produced/lb BOD removed

b = 0.08 = endogenous rate of sludge oxid./day

Lr = BOD removed

c Lbs volatile solids produced/day = 0.55Lr - 0.08MLVSS

d Oxygen uptake rate (mg/1/hr)

$$= \frac{\text{lbs } O_2\text{/day}}{24\ \text{Va}}$$

where: Va = aeration tank capacity in million lbs water

2 1970 Concepts

a BOD loading factor = $\frac{F}{M} = \frac{24\text{So}}{\text{Xat}}$

where: F = food
M = microorganism mass
So = influent BOD in lbs/day
Xa = average MLVSS
t = aeration time in hrs.

b Substrate removal rate coefficient

$$k = \frac{So - Se}{XatSe}$$

where: Se = effluent BOD

c Lbs 0_2/day = a'Sr(Q/V) - b'Xa

= QKi + aSrQ - (bXaV + QXe) (oxygen basis)

where: a' = fraction BOD oxidized
b' = fraction VSS oxidized

d Lbs sludge produced/day

where: Q = waste flow
Xi = influent SS
Xe = effluent SS
a = fraction BOD converted to cells
b = fraction VSS oxidized (dry solids basis)

e Simultaneous equations are used to estimate unknowns. Experimental data may require alteration of certain equation components. It is usually advisable to design for the longer of the aeration time estimates.

Determination of constants

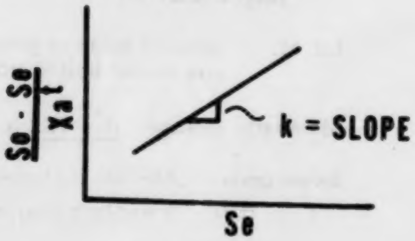


FIGURE 1

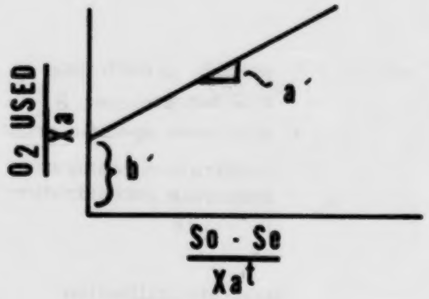


FIGURE 2

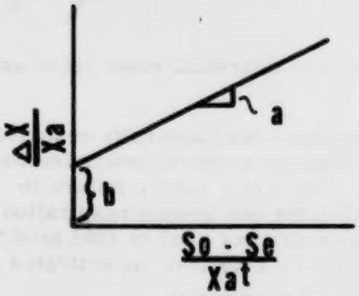


FIGURE 3

where: data are obtained from variable loadings

C Modified Monod Equations

1 In 1942, Monad developed set of empirical equations to approximate pure culture bacteria growth.

2 In 1950, Monad expanded his equations to continuous feed systems.

a Mass growth

$$\ln(X/Xo) = (\mu - D)t$$

where; X = microbial mass at time t
Xo = initial microbial mass
μ = specific growth rate
D = dilution rate
t = reaction time

b Specific growth rate (μ)

$$\mu = \mu_o \frac{S}{S_k + S}$$

where: μ = specific growth rate at substrate conc. S
μ_o = maximum specific growth rate
S = substrate concentration
S_k = substrate concentration when $\mu = \mu_o/2$

c Substrate utilization

$$\frac{dS}{dt} = D(So - S) - \frac{X}{R}\left(\mu_o \frac{S}{S_k + S}\right)$$

where: R = microbial mass yield constant

3 Popular with University researchers
4 Problems arose in determination of μ_o, R, and S_k and in failure to consider endogenous respiration.
5 Reynolds and Yang in 1966 modified Monod's equations for activated sludge

a Required MLSS (X)

$$X = \frac{Y(So - S)}{1 + \alpha - \alpha\left(\frac{1 + \alpha}{\alpha + w}\right) + Ket}$$

where: Y = sludge yield coefficient
α = sludge recycle ratio
w = waste sludge ratio (fraction of raw waste)
Ke = endogenous respiration rate

b Desired aeration time (t)

$$t = \frac{1}{XKe}\left\{Y(So - S) - X\left(1 + \alpha - \alpha\left(\frac{1 + \alpha}{\alpha + w}\right)\right)\right\}$$

c Oxygen uptake rate

$$\frac{dO}{dt} = (1 - 1.42Y)\,\frac{So - S}{t} + 1.42\,KeX$$

d Determination of Ke, Y, u_o, and S_k

D Complete Mixing Equations

1 First applied to activated sludge by Garrett & Sawyer in 1952 laboratory evaluation (6).

2 The first detailed set of design equations for complete mix activated sludge (CMAS) plants, was published in 1962 (7) and modified in 1969 (8).

a Organic reduction

$$F = \frac{Fi}{Kmt + 1}$$

where: F = unmetabolized BOD (available BOD at any given time)
Fi = influent BOD
Km = metabolism factor (15βhr @ 20°C)
t = aeration time in hrs

b Active microbial mass

$$MA = \frac{KsF}{\frac{1}{ts} + Ke}$$

where Ma = active microbial mass (mg/1 MLVSS)
Ks = synthesis factor (10.4/hr @ 20°C)
ts = sludge retention time in hrs.
ke = endogenous respiration factor (0.02/hr @ 20°C

c Endogenous mass

$$Me = 0.2KeMats$$

where: Me = endogenous mass (mg/1 MLVSS)

d Inert Organic mass

$$Mi = Inf.\ Mi(ts/t)$$

where: Mi - inert organic mass (mg/1 MLVSS)

Inf. Mi = influent inert organic suspended solids (mg/1 VSS)

(domestic sewage: 0.4 VSS in influent

Experience: .20-.40 20 years ago
.4 works better now

e Inert Inorganic mass

$$Mii = Inf.\ Mii\ (ts/t) + 0.1\ (Ma + Me)$$

where: Mii = inorganic MLSS (mg/1)
Inf. Mii = influent inorganic suspended solids (mg/1)

f Total MLSS

$$M_T = Ma + Me + Mi + Mii$$

g Oxygen Uptake rate

$$\frac{dO}{dt} = \frac{1.5(Fi - F)}{t} - \frac{1.43(Ma + Me)}{ts}$$

where: $\frac{dO}{dt}$ = oxygen uptake rate (mg/1/hr)

h Temperature effect

Km, Ks, and Ke change by factor of 2 with 10°C change (over a temp range of approximately 10-35°C)

i Determination of Km, Ks, and Ke laboratory and field data

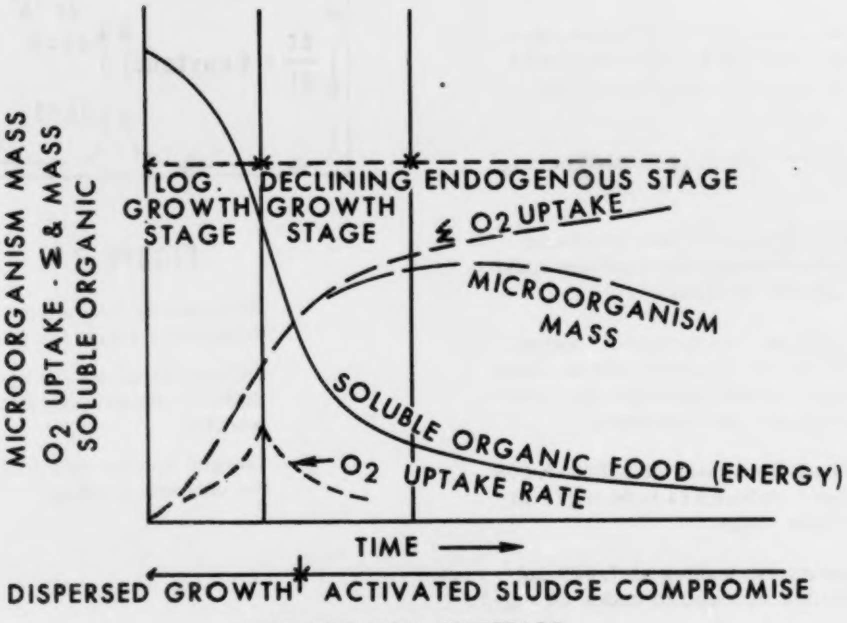
E Application of design equations

1 There is considerable confusion as to application to real systems.
2 All 3 sets of equations can yield reasonable design criteria. How the equations are used is more important than which one.
3 Eckenfelder and Monod equations empirical and require separate evaluation for each waste.
4 CMAS equations developed from fundamental microbial concepts

a Declining growth phase only (food limiting)
b Single set of design factors for all wastes through evaluation of Ma, Me, Mi, and Mii
c Variations in design factors related to types of microbes

1 Bacteria-protozoa yield optimum results
2 Fungi yield more cell synthesis and less oxidation
3 Proper environmental design insures proper microbes

FIGURE 6



IV PLUG FLOW VS COMPLETE MIXING (9)

A Longitudinal mixing

1 Conventional activated sludge uses long, narrow aeration tanks with spiral flow aeration to minimize longitudinal mixing.

2 Horizontal velocity approx. 5 fpm along the tank axis.

3 Normally, length to width ratio in excess of 5:1.

4 Axial dispersion concepts used in 1963 to evaluate mixing.

5 Existing studies indicate that current activated sludge tanks are neither plug flow nor completely mixed in spite of a rash of reports that existing aeration tanks are completely mixed.

B Complete mixing

1 Developed in Bury, England, 1919, then built plants long and narrow.

2 First real use was with extended aeration systems in 1950.

3 Fundamental microbial research at MIT in 1950's indicated that CMAS was preferred from a microbial point of view.

4 Laboratory and field studies during past 20 years confirm this.

5 Field CMAS plants have produced results not attainable with any other biotreatment system.

a Alkaline cotton textile wastes, pH 10-11, treated without chemical preneutralization and minimal nutrient additions.

b Phenolic wastes at 2,000-3,000 mg/1 reduced to 0.04 mg/1 in single stage.

c Antibiotic wastes at 7,000 mg BOD/1 reduced to under 50 mg/1.

d Shock loads handled with no significant impairment in effluent quality up to 2-3 times average BOD load.

6 Any desired effluent can be produced from any influent concentration.

7 Not readily accepted by engineers initially for fear of short circuiting.

8 Computer studies by University professors on CMAS vs plug flow indicated CMAS not as efficient as plug flow.

9 CMAS slowly being accepted by engineers.

10 Largest CMAS plant currently under construction is 100 MGD plant at Rochester, New York.

11 CMAS is not instantaneous mixing, arbitrarily defined as having a one minute mixing time at high loading.

12 Fluid flow pattern.

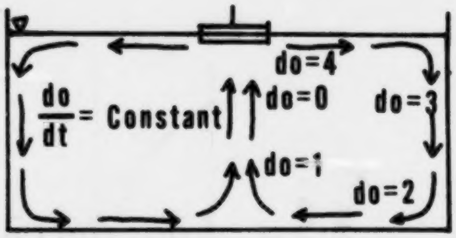


FIGURE 7

SS measurements not accurate enough for use

DO varies along the circulation pattern; lowest on return to the aerator.

Oxygen uptake rate is constant for uniform loading.

13 CMAS most efficient and most economical biotreatment system currently in use and can meet any reasonable effluent BOD requirement.

V AERATION SYSTEMS

A Turbine aeration

1 Diffused air added under turbine.

2 Diffused air establishes fluid flow pattern, not the turbine.

3 Quirk in 1962 found optimum results when air blower power equaled turbine power.

4 Transfer 2.5 to 3.0 lbs 0_2/HP/hr with 20% efficiency.

5 A turbine requires 50% more power when pumping liquid than when pumping a less dense mixture of liquid and gas.

6 Surface aerator above the turbine is not an efficient design.

B Surface aeration

1 General acceptance of surface aeration in the United States has been slow. Diffused air systems were popular and early attempts at surface aeration were penalized by large safety factor regulations. Both designs of units and concepts have improved.

2 The surface aerator essentially is a fluid pump designed to create a large gas-liquid interface area and fluid mixing energy.

3 Maximum oxygen transfer efficiency occurs when the pumped fluid is saturated with oxygen as it leaves the aeration device and returns to it with a large oxygen deficit. Microbial viability constraints require that returning fluid DO > 0.

4 Oxygen transfer relationships:

$$\frac{DO}{dt} = K_{La}\,(0_S - 0_L)$$

where: $\frac{DO}{dt}$ = the change in DO per unit time.

K_{La} = The oxygen transfer coefficient
= A measure of turnover time for fluid to be saturated with oxygen.
= Q_s/V under conditions where Q_s or quantity of fluid flow saturated with oxygen
= Q_w or quantity of fluid flow pumped. (maximum transfer).

V = Pump flow rate.
Fluid turnover time = V/Q_w

O_S = the oxygen saturation value for the fluid under test.

O_L = the DO value of the liquid returning to the aeration device.

5 Draft tubes and baffles help to direct flow properly and improve mixing.

a A draft tube orients upward fluid flow to the surface aerator, maintains solid suspension and minimizes dead spots of low DO fluid at the bottom of the tank.

b Baffles tend to break up centrifugal momentum of tank contents that may produce short circuiting.

6 Surface aerator performance depends upon the nature of the liquid, the unit, its size, loading, and tank geometry. The oxygen transfer capabilities at maximum loading are most important. For example: With similar devices.

a 3.0 to 4.0 lbs 0_2/HP/hr may be transferred in pure water.

b 2.5 to 3.0 lbs 0_2/HP/hr may be transferred in mixed liquor.

c 1.5 to 2.0 lbs 0_2/HP/hr may be transferred in large aerated lagoons.

C Rotor aeration

1 Developed in Holland as modification of Kessener brush.

2 Current design: 28" dia. rotor with 12 rows of 2x6" flat tabs @4" centers.

3 At 70 RPM with 3 to 6" submergence 2.5-4.0 lbs 0_2/HP-hr may be transferred.

4 A modification at the University of Kansas resulted in a 60" dia. rotor which can transfer between 4.0 and 5.0 lbs 0_2/HP-hr.

5 These units are more specialized than other aerators with primary use in shallow tanks.

D Pure oxygen

1 Increased driving force and higher saturation level are the main factor.

2 Early studies by Okun not economically feasible.

3 Studies at the University of Kansas in the 1960's demonstrated value of pure oxygen lay with partial pressure and oxygen demand. Without a high oxygen demand rate, it was not economical.

4 Recent interest revived by Union Carbide study at Batavia, N.Y.

5 Contrary to Batavia reports, there is no fundamental basis for lower sludge production in pure oxygen in contrast to air provided adequate air is supplied. With limited air, endogenous respiration seems to be suppressed and metabolism of adsorbed suspended solids are retarded, both resulting in higher than normal sludge production.

6 A properly designed CMAS plant with mechanical surface aeration unit is more economical than pure oxygen at present time both in capital and operating costs.

VI HIGH MLSS SYSTEMS

A Recent trend is toward higher MLSS concentrations, 4,000 - 6,000 mg/l.

B Extended aeration plants with 5,000 - 10,000 mg/l MLSS started trend in effort to reduce frequency of sludge wasting.

C Eckenfelder's equations indicated a MLSS-time relationship. Aeration time could be shortened with increased MLSS for the same effluent quality.

D CMAS equations indicated short aeration times would require high MLSS concentrations but effluent quality would decrease.

E High MLSS concentrations require sludge return with weak organic wastes but not for concentrated wastes. Domestic sewage and normal activated sludge require 100% sludge return rate based on raw waste flow for 5,000 mg/l MLSS and 200% for 6700 mg/l.

F Inert solids in raw waste determine inert solids in mixed liquor. Both inert organic and inert inorganic suspended solids build up in mixed liquor. Domestic sewage normally contains 125 mg/l of inert suspended solids. Primary sedimentation will remove this 125 mg/l down to 50 mg/l while chemical coagulation can reduce it to less than 10 mg/l.

G High MLSS concentration systems require special sedimentation tanks to prevent excessive solids loss in effluent.

H Current design should limit MLSS to lowest level based on microbial mass for peak organic loads, 2,000 - 4,000 mg/l MLSS. High solids are likely to require higher aeration cost than are saved by reduction of sludge solids for disposal.

VII OXIDATION DITCH

A Developed by Paasveer in Holland for small extended aeration systems.

1 Utilize a rotor aerator for agitation and creation of air-liquid interface area.
2 Employs a shallow oval ditch as a fluid container.
3 Depth of ditch limited by fluid pumpage and minimum velocity to keep sludge in suspension, (1.0 fps).
4 Distance between rotors determined by oxygen demand rate and time of flow.

B The oxidation ditch has become popular for animal feedlot waste treatment.

1 Hogs and beef cattle are grown on slotted floor directly above the ditch.
2 Concentrated urine and manure drop directly into ditch along entire length for relatively uniform feeding.
3 Hog manure has BOD of 40,000 mg/l which must be diluted by treated wastes in ditch if the system is to remain aerobic.
4 Rotors spaced at intervals depending upon the total manure load and time of travel between rotors.
5 High nitrogen content of manure and urine, long aeration periods, and excess DO produces nitrification.
6 As organic load increases, oxygen demand exceeds available DO and denitrification results with loss of nitrogen. At full organic load, it is possible to obtain essentially complete nitrification and denitrification.
7 The oxidation ditch potential is just beginning to be realized.

VII SOLIDS SEPARATION

A The effluent quality of activated sludge systems are determined by effluent suspended solids.
B The present trend is to reduce surface overflow rate to prevent suspended solids loss but with a constant retention period, the depth is reduced.
C With high MLSS, the trend to shallower final sedimentation tanks is an invitation to disaster.
D Concern is centered on the rapid removal of activated sludge from the sedimentation tank.

1 Hydraulic sludge collection devices have been developed, but return sludge concentrations are difficult to control.

2 Units operate best at 6,000 mg/l suspended solids or less.

3 They require high return sludge rates for proper MLSS in aeration.

4 They require separate sludge thickening system for waste activated sludge.

5 High sludge return rates result in mixed liquor displacement from the aeration tank creating turbulence in the sedimentation tank.

6 Turbulence is a definite problem in shallow units.

7 Sludge retention time in final sedimentation tank actually is the same as the corresponding fluid retention time.

8 No real advantage in hydraulic sludge return system over properly designed unit.

E Conventional sedimentation tanks.

1 Normal concentration in gravity unit and sludge scrapers is 10,000 mg/l.

2 Higher sludge concentrations than 10,000 to 12,000 mg/l indicates excessive storage in sedimentation tank and definite sludge deterioration or higher than normal fraction of inert inorganics.

3 Minimum MLSS concentration results in minimum return sludge and minimum turbulence at inlet to the sedimentation tank.

4 With HIGH MLSS, the sedimentation tank will be at least half full of sludge at all times regardless of sludge collection mechanisms.

5 Sludge retention time the same as corresponding fluid retention time.

6 The volume of sludge in the sedimentation tank points up need for deep tanks.

7 All final sedimentation tanks should be equipped with scum removal equipment and scum baffles around wiers.

F Waste activated sludge should be handled separately from primary sludge.

1 Mixing with primary sludge adversely affects primary sludge dewatering.

2 Waste activated sludge is difficult to concentrate or dewater directly as a result of the structure of the microbial cells and hydration of them.

3 Large quantities of chemicals needed to overcome organic characteristics of activated sludge.

VIII AEROBIC SLUDGE DIGESTION

A Waste activated sludge aerobic digestion.

1 Used in extended aeration and package contact stabilization plants. Part of the digestion has occurred in process.

2 Only active mass can be digested up to maximum of about 80%.

3 Stabilization rate: 2%/hr at 20°C, 1% @ 10°C and 4% @ 30°C.

4 A series of compartments in digestion tank produces plug flow and maximum sludge digestion.

B Primary sludge

1 Reactions are the same as in regular activated sludge aeration tank including rapid metabolism followed by endogenous respiration.

2 Similar to animal manure treatment.

3 Need dilution below oxygen transfer limitations.

4 After 80-90% reduction in active mass sludge, the fluid concentrates by gravity to above 5% and dewaters rapidly.

IX CURRENT DESIGN CRITERIA

A Domestic Sewage

1 Normal flow and BOD variations favor CMAS systems.

2 Any of the 3 sets of mathematical equations will work satisfactorily.

3 Major problem is sludge handling. Every effort should be made to minimize sludge production, reducing sludge disposal to a minimum.

4 Design of any waste treatment system is not complete until all solids are returned to land and fluid returned to the water environment.

5 Trend to short aeration time results in excessive sludge production.

6 With domestic sewage, 3 hours appears to be normal lower limit for aeration time to produce satisfactory effluent at all times and absorb peak loads.

7 Reducing the aeration tank detention below 3 hours is false economy as increased operational costs and equipment costs will override the small savings in aeration tank volume.

8 Oxygen equipment must be designed to meet peak oxygen demand in mixed liquor and not average oxygen demand in pure water. Valid performance specifications are essential for aeration equipment.

9 Phosphate removal can be accomplished best by a combined chemical biological system employing coagulant ahead of primary sedimentation tank to remove maximum quantity of primary sludge prior to aeration. Activated sludge removes residual phosphate with chemical ppt as final polisher if needed.

10 Reduction in aeration costs and sludge handling costs will offset chemical cost for phosphate reduction.

11 Ammonia stripping and low BOD effluents are not compatible.

12 Complete nitrification requires long sludge retention time, over 5 days, with 50% excess oxygen and adequate buffer to keep pH over 6.5.

13 Mechanical surface aeration is the most economical system at present.

14 Aeration systems must be designed to handle peak loads based on actual oxygen uptake rates.

15 Final sedimentation tanks can produce good results at 800 gal/sq.ft./day surface overflow rate with minimum depth of 12 ft.

16 Variable sludge return capability between 25 and 100% based on raw waste flow are essential. Adequate measuring devices also are necessary for control.

17 Sludge wasting should be continuous where possible from the return sludge stream.

18 Waste activated sludge should not be returned to primary sedimentation tanks or anaerobic digesters if at all possible.

19 Aerobic sludge digestion is the best volume reduction method with 15-20 day aeration required, including the sludge retention time in the activated sludge aeration tank.

B Industrial Wastes

1 No fundamental difference in design for domestic sewage or industrial wastes. In both cases, the system must be designed on the basis of the available food energy in process, the oxygen uptake rate exerted and the amount of working biological solids. Total suspended solids carried in process depend upon inert residues, time energy relations, and effluent quality sought.

2 The pH of raw waste important only as it affects pH of mixed liquor. Keep pH between 6.5 and 9.5 in the mixed liquor.

3 Surge tanks help level load variations and produce a better effluent.

4 CMAS systems are best able to handle shock loads that occur from time to time.

X CURRENT OPERATIONAL CRITERIA

A Without good operation, the best design is of little value.

B The current trend toward complex, automated, highly instrumented controls with infinite variability are undesirable. Design should minimize mechanical equipment.

C Mechanical equipment should be selected for ease of maintenance, reliability, long life, and ease of replacement.

D DO control unnecessary but time clock adjustment at 8 to 12 hour intervals can assist in economical control.

E Constant rate of sludge return simplifies operation and produces best results.

F CMAS aeration tanks produce uniform oxygen demand within limits and permit use of constant speed mechanical aerators.

G Solids level control in sedimentation tank and balance between BOD load, sludge wasting, and oxygen utilized permits easy operational evaluation.

XI RECOMMENDED DESIGN FOR DOMESTIC SEWAGE

A CMAS system.

B 3 hrs aeration based on raw waste flow.

C Constant speed mechanical aerator.

D Constant rate of sludge return.

E Constant rate of sludge waste.

F Return sludge to land and water to environment.

G Simplicity of design and operation can produce an effluent with 20 mg/l BOD and 20 mg/l SS without difficulty, 10 mg/l BOD and 10 mg/l SS with a little effort, and 5 mg/l BOD and 5 mg/l SS with close control of design and operation.

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FUNDAMENTALS OF TRICKLING FILTRATION WASTE TREATMENT

I INTRODUCTION

Trickling filters are not filters at all, but basically only a pile of rocks providing surface area upon which slime organisms grow. These organisms feed on the dissolved food matter contained in the waste effluent applied to the filter. When too thick a slime growth accumulates, anaerobic conditions develop at the media surface. A natural mechanism for cleaning the filter occurs with the periodic "sloughing" of the slime layer from the surface of the filter media. Solids that are sloughed off are collected by final clarification of the filter effluent.

As waste passes through the filter, nutrients and oxygen are transferred to the slimes, where assimilation occurs, and by-products and CO_2 are transferred out of the slime into the flowing liquid. As oxygen diffuses into the biological film, it is consumed by microbial respiration so that a defined depth of aerobic activity is developed. Slime below this depth is anaerobic.

In a manner analogous to activated sludge such as the contact stabilization mode, BOD removal through a trickling filter is related to the available biological slime surface, its activity and to the time of contact of waste with that surface.

II TRICKLING FILTER COMPONENTS AND THEIR FUNCTIONS

A Distribution - rotary or fixed nozzle

Intermittent waste application, wets all media surfaces, applies effluent uniformly.

B Media or Packing

Supports slime growth, and intimate contact of slime - wastewater - air.

1 Conventional filters contain 2-1/2 - 4 inch rock packing and vary in depth from 3 - 8 feet. Hydraulic loadings to the filter of 0.5 gpm/ft^2 will yield BOD removal efficiencies up to 85%.

2 Plastic packings, such as Surfpac, are employed in depths up to 40 feet with hydraulic loadings as high as 4.0 gpm/ft^2. Depending on the hydraulic loading and depth of the filter, BOD removal efficiencies as high as 90% have been attained on strong wastes.

C Underdrainage System

Collects and conveys effluent, admits or draws off air, supports filter media.

D Secondary Clarifier

Provides separation of agglomerated solids and sloughed slime growths from final effluent. Final clarifier overflow rate varies between 800-1000 gallons per day per square foot (gpd/sq ft).

III ADVANTAGES AND LIMITATIONS OF THE TRICKLING FILTRATION PROCESS

A Advantages

1 Relatively high nitrifying effect upon effluent

2 Low operating cost

3 Ability to function under extreme weather conditions

4 Good efficiency in BOD_5 removal

5 Good efficiency in suspended solids removal

6 More complex biota than for activated sludge

B **Limitations**

1 High head losses

2 Odor and fly nuisances

3 Large land area required

4 High initial construction cost

5 Head losses may require pumping

6 Forced ventilation may be necessary

IV CLASSIFICATION OF TRICKLING FILTERS

A Low Rate or Standard Trickling Filters

1 Hydraulic loading

1.1 - 4.4 million gallon per acre per day (mgad) 25 - 100 gpd/sq ft

2 Organic loading

220 - 1,100 lbs BOD_5/acre-ft/day
5 - 25 lbs BOD_5/1000 cu ft

3 Recirculation - usually not

4 Filter depth - 5 - 10 ft (ave. 7')

Most of the very early filters were of this type.

B High Rate Trickling Filters

1 Hydraulic loading

8.7 - 44.0 mgad
200 - 1000 gpd/sq ft

2 Organic loading

1,100 - 13,000 lbs BOD_5/acre - ft/day
25 - 300 lbs BOD_5/1000 cu ft

3 Recirculation - normally provided

4 Filter depth - 3-7 ft (ave. 5')

Most of the filters constructed in recent years have been high-rate filters. These filters were built with various depths, and organic loadings.

The performance of biological treatment units of this type is dependent upon the volume of ACTIVE growth present in and on the filter media. The size of the filter and the type of filter media determine the amount of space available for the growth of the biological slime mass.

The rate of application of the waste influences the amount of growth that will develop. The two types of loading (i.e. organic loading and the volumetric or hydraulic loading) have opposite effects. The greater the amount of available organic matter, the greater the food supply and expected growth. Recirculation increases trickling filter efficiency. High dosage rates however increase scour, dislodge slime growth, and reduce the volume of active growth present in and on the filter media. It is noted that organic loading has greater influence on trickling filter efficiency than hydraulic loading.

C Super Rate or Roughing Filters

1 Hydraulic loading - up to 1000 mgad

2 Organic loading - (see comment noted below)

3 Recirculation - normally provided

4 Filter depth - up to 40 feet using manufactured plastic filter media instead of rock or stone

This process is usually associated primarily with treatment of industrial wastes.

In recent filter design, organic loadings greater than those listed above for the high-rate filters have been applied. This is particularly true when manufactured filter media is used. Presumably the ratio of the useful surface area of the media to the volume of the media is greater, resulting in higher efficiency of BOD_5 removal per unit volume of filter.

Manufactured filter media provide a much greater surface area for slime growth per unit volume than rock or slag. Greater ventilation possibilities are inherent.

V DESIGN CONSIDERATIONS FOR TRICKLING FILTRATION SYSTEMS

A Common Flow Diagrams

Figures 1 and 2 show the more common flow diagrams and operational variations for recirculation of solids and effluents associated with trickling filtration waste treatment.

B Factors in Trickling Filter Design

It appears that the efficiency of a trickling filter is dependent upon all or some of the following variables:

1 Composition and characteristics of the waste

2 Organic loading

3 Pretreatment by sedimentation or other processes

4 Hydraulic loading; recirculation ratio and system.

5 Filter bed characteristics; volume, area, and depth

6 Type of filter media selected

7 Aeration or forced ventilation

8 Wastewater and air temperature

C Pretreatment Requirements

1 The BOD applied to the filter should generally not exceed 500 mg/l in order to insure aerobic conditions. Recirculation should be employed when wastes have BOD_5 values much in excess of this value.

2 When a filter packing with a high specific surface is used, a minimum hydraulic loading is essential to avoid the accumulation of excessive biological growths and resulting filter ponding.

3 The pH of the wastewater applied to the filter should be such that the excess alkalinity or acidity is neutralized in the top few feet of the filter media. Excessive acidity or alkalinity can frequently be neutralized by recirculation of filter effluent.

D Effects of Recirculation

1 Part of the organic matter in the raw waste feed is brought into contact with the slime organisms more than once.

2 High concentration wastewaters are diluted before contact.

3 Recirculated effluent contains active microorganisms not found in such quantity in raw waste, thus providing seed continuously.

4 Diurnal organic waste loadings are distributed more evenly.

5 The continuation of waste application to the filter during periods of low flows (night time) precludes long detention periods which may result in septicity. Stale sewage is freshened. Slimes do not dry out.

6 Increased hydraulic loading through recirculation improves uniformity of waste distribution, increases sloughing, and reduces clogging tendencies.

7 Higher velocities and continual scouring also produces conditions less favorable for the growth of filter flies.

8 Continual seeding with active slime organisms and enzymes stimulates hydrolysis and oxidation and increase the rate of biochemical stabilization of the waste.

TRICKLING FILTER

FLOW AND RECYCLE

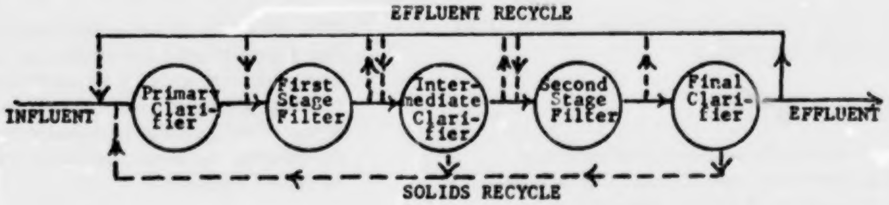

EFFLUENT RECYCLE
INFLUENT
Primary Clari-fier
First Stage Filter
Inter-mediate Clari-fier
Second Stage Filter
Final Clari-fier
EFFLUENT
SOLIDS RECYCLE

Figure 1

TRICKLING FILTER

FLOW AND RECYCLE

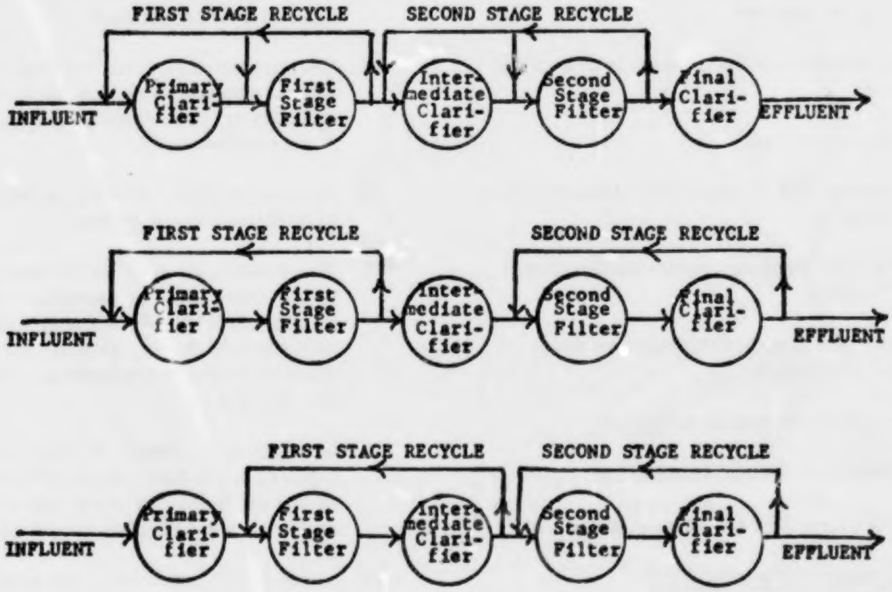

FIRST STAGE RECYCLE
SECOND STAGE RECYCLE
INFLUENT
Primary Clari-fier
First Stage Filter
Inter-mediate Clari-fier
Second Stage Filter
Final Clari-fier
EFFLUENT
FIRST STAGE RECYCLE
SECOND STAGE RECYCLE
INFLUENT
Primary Clari-fier
First Stage Filter
Inter-mediate Clari-fier
Second Stage Filter
Final Clari-fier
EFFLUENT
FIRST STAGE RECYCLE
SECOND STAGE RECYCLE
INFLUENT
Primary Clari-fier
First Stage Filter
Inter-mediate Clari-fier
Second Stage Filter
Final Clari-fier
EFFLUENT

Figure 2

9 Recirculation will increase operating costs because of the necessary pumping of the return effluent.

10 Wastewater temperatures may be reduced as a result of the number of passes of the liquid through the filter. During cold weather, this may result in decreased biochemical activity and reduced efficiency of treatment provided.

VI FILTER OPERATION AND MAINTENANCE

A Maintenance of Equipment

Requirements vary somewhat with each piece of equipment. Specific instructions should be obtained from the manufacturer. Common requirements usually include the following:

1 Top bearing

  a Add grease monthly

  b Remove, inspect, clean, and lubricate with new grease once each year.

2 Lower bearing

  a Ball bearing--check oil level monthly

  b Roller bearing--add oil or grease monthly

  c Mercury seal--drain, inspect, and check quantity once each year. Add mercury when necessary. Check as needed under contingency conditions.

  d Oil seal--check and add oil as required. Drain, inspect, and replace oil at least once each year and seasonally where required.

3 Guy rods--in cold weather it may be necessary to loosen guy rods in order to prevent arms from being raised at the outer end. In warm weather tighten guy rods to prevent arms from dragging on the stone.

4 Freezing--when there is danger of freezing, gates at ends of arms may be left partly open to drain the distributor. This is not required where distributors operate continuously.

5 Closing down--whenever it is necessary to shut the distributor off for any extended length of time, the drain valve in the base ell should be opened.

B Plugging of Filters--"Ponding" of filters may occur if prolific growths develop completely filling voids between the rocks or if leaves, trash, or plastics accumulate in the bed. One or more of the following methods may be used to reduce or eliminate plugging:

1 Flush the surface of the filter with a fire hose, simultaneously loosening rock with a bar as the jet is applied.

2 Rake or fork the surface.

3 Stop the distributor over affected areas, and allow the flow of sewage to wash down growths and sludge. This is applicable if bed is not completely sealed.

4 Apply heavy doses of chlorine or chlorinated lime in the filter influent in concentrations up to five mg/l residual for periods of two to four hours at intervals of two or three days. This should be done at night when flow is light and chlorine requirement is low.

5 Flood the filter and allow to stand 24 hours.

6 Dry the filter by taking it out of service for 12 to 48 hours and exposing it to sunlight. This should be done only if other units are available to provide adequate treatment capacity.

7 Under no condition should heavy equipment be allowed on the filter surface. The weight will cause damage to the walls, crust filter aggregate and cause damage to underdrain systems, cause further ponding, and require extensive

repairs and replacements. Heavy equipment must be supported by planking to distribute load.

8 In cold climates, keep the surface of the filters sufficiently free of snow to permit operation of rotary distributors. Leaves and other wind-blown material should not be allowed on the filter. Removal of trees from areas nearby may be necessary. Promptly remove surface paper leaves plastic-wind-blown or water carried.

C Filter Flies - Breeding in filters is minimized where there is continuous heavy uniform application of liquor to the stone and wall surfaces, provided sludges do not accumulate. Pupae and larvae develop under favorable operating conditions, but in high rate filter units they are continuously washed into the final settling tank. In the standard filter, particularly with intermittent operation, flies may become a nuisance. The distribution from center to outside walls. One or more of the following control measures may be utilized.

1 Vigorous hosing of inside filter walls.

2 Flooding the filter. The filter flies seem to prefer a damp but not a wet environment. The filter should be flooded for 24 hours at intervals of ten days to two weeks depending upon the hatching cycle. Filter efficiency may decrease temporarily following such flooding, but it will be regained in a reasonable length of time.

3 Cut all grass and weeds around filters.

4 Use of DDT--washing or spraying filter walls with a five percent solution DDT insecticide in kerosene will effectively kill all contacted adult flies. This should be started early in the season and be repeated each six weeks. This procedure has been used successfully to reduce flies below the nuisance level and has had no deleterious effect upon the operation of the filter. Check use regulations first.

D Control of Odor - Odors from filters are due to undesirable growths, sludging, and anaerobic decomposition. Odors can be eliminated by preventing such conditions from developing. The following methods are recommended:

1 Where the sewer system is extensive or grades flat, sewage may undergo decomposition before reaching the plant. Aeration or chlorination of sewage in the upper part of the collection system will freshen the raw sewage plant influent and reduce odors. The trickling filter influent may also be aerated to oxidize organic overloads, eliminating anaerobic conditions within the filter which result in hydrogen sulfide production and odors.

2 Recirculation of filter effluent may also be used to promote aerobic conditions.

3 Promote good housekeeping and maintain a washdown schedule to aid plant cleanliness.

E Records of Operation

Plant records should include the following:

1 Rate of recirculation to filter, if any, and source of recirculated material.

2 Record of cleaning spray or distributor nozzles.

3 Record of mechanical maintenance of filter distributor and appurtenant mechanisms.

4 Remarks covering any unusual condition or operation correction of ponding, fly breeding, odor control, snail infestation, etc., as effected by chlorine application, flooding, washing, etc.

5 Complete laboratory analysis as required.

ACKNOWLEDGEMENT:

Portions of this outline were taken from a previous outline prepared by Quintin B. Graves, Professor of Civil Engineering, School of Civil Engineering, Oklahoma State University, Stillwater, Oklahoma

This outline was prepared by James A. Montgomery, Sanitary Engineer, River Basin Planning, Water Program Operations, Washington, DC 20242.

THE DESIGN OF TRICKLING FILTRATION SYSTEMS

I INTRODUCTION

A The Future Outlook for Trickling Filtration Waste Treatment

1 Larger cities are turning more and more towards activated sludge waste treatment systems as they realize the limitations of trickling filtration in satisfying future water quality standards. When competent operation and steady-state waste flow conditions are provided, activated sludge will generally produce a higher quality effluent.

2 Trickling filtration systems will continue to be designed for the smaller cities where full-time operation is not provided. Trickling filters will normally operate at 80 to 90 percent BOD_5 removal efficiency. Their effluent is expected to be somewhat turbid as compared to activated sludge effluent in which 90 to 95 percent BOD_5 removal is achieved.

3 Trickling filtration units will also continue to be utilized in treatment plant expansions as "roughing filters" to equalize and partially reduce high organic waste flows for further waste treatment processes.

B Design Methods to be Considered in this Outline

1 "Ten States Standards"--general requirements

2 Conventional Design Method

3 National Research Council (NRC) Formula

4 Eckenfelder Formula

5 Galler -- Gotaas Formula

II "TEN STATES STANDARDS"

The Great Lakes - Upper Mississippi River Board of State Sanitary Engineers has formulated policies for the review and approval of plans and specifications for sewage collection and treatment facilities. Their publication, Recommended Standards For Sewage Works commonly referred to as "The Ten States Standards," is currently used by most state water pollution control agencies as a guide for accepted design practices.

This publication may be obtained from the Health Education Service, Post Office Box 7283, Albany, New York 12224. The cost is $1.00 per copy. TABLE 1 which follows, outlines the more important general requirements for the design of trickling filtration systems contained in this publication:

III CONVENTIONAL DESIGN METHOD

Trickling filtration systems may be classified as "Low Rate" or "High Rate" filters according to their organic and hydraulic loadings. Accepted design ranges for each class of filters are given in TABLE 2. Examples showing how this information may be used to design each class of filters will now be considered.

A Design of Low-Rate Trickling Filter

Example 1

Given:

Sewage Flow Rate (Q) = 10 mgd

BOD_5 in Raw Waste = 200 ppm

BOD_5 Removal in Primary Settling Tank = 30%

Problem:

Design a filter system and check for acceptability

TABLE 1

TRICKLING FILTER DESIGN - 10 STATES STANDARDS

Point Under Review	Standard	Reference
Does a check of the hydraulic factors involving distribution show these to be satisfactory? For rotary type there should be 24" minimum head between low level in siphon and center of arms.	yes	71.23
Is the apparatus or system for distribution one which normally results in uniform distribution of sewage over the filter bed surface?	yes	71.21
Is the clearance between the surface of the filter and the distribution arm of the rotary distributor satisfactory?	6" min.	71.24
Do the specifications describe satisfactory media material?	yes	71.31
Is the size of media satisfactory?	yes	71.33
What is minimum depth of media above the underdrains?	5 ft.	71.32
What is maximum depth of filter media?	7 ft.	71.32
Do specifications require that the media be laid in such a manner as to minimize abrasion?	yes	71.334
Do specifications require that media be hand laid for the first 12" above the underdrains?	yes	71.334
Do the underdrains cover the entire floor of the filter?	yes	71.41
Is the unsubmerged gross combined area of the inlet openings into the underdrains satisfactory?	15% of surface area of filter	71.41
Is the slope of the underdrains satisfactory?	1% min.	71.42
Is the velocity in effluent channels at average daily rate of application satisfactory?	2 ft/sec min.	71.42
Is provision made for flushing underdrains? For small filters a peripheral head channel is acceptable.	yes	71.43
Is inspection provided for?	yes	71.43
Are the underdrains and effluent pipe designed to provide free passage of air?	yes	71.44
Is the size of the underdrains satisfactory? No more than 50% of the cross sectional area should be submerged under design loading?	yes	71.44
If filter is of the standard rate type, has consideration been given in the design to the possibility of the filter being used later for high rate filtration?	desirable	71.44

TABLE 1 (Continued)

TRICKLING FILTER DESIGN - 10 STATES STANDARDS

	Standard	Reference
Standard Rate Filters		
If filter is classified as a standard rate type, are the loadings within these limits?		**
1.1 to 4.4 million gals. per acre per day.	yes	
5 to 25 lbs. BOD_5 per 1,000 cubic ft. per day.	yes	
The allowable reduction in BOD for a given standard rate filter followed by a settling tank can be obtained from Figure 2 in the Ten States Standards.		71.7
Has the filter been designed to provide the BOD reduction required for a satisfactory effluent?	yes	71.12
Has consideration been given to recirculation?	yes	71.56
High Rate Filters		
If filter is classified as a high rate type, are the loadings within these limits?		
8.7 to 44 million gals. per acre per day.	yes	**
25 to 300 lbs. BOD_5 per 1,000 cubic feet per day.	yes	**
Is recirculation provided to maintain a continuous dosing rate of at least 8.7 million gallons per acre per day?	yes	**
Does the distribution system provide continuous discharge to the filter, giving no rest period in excess of 15 seconds?	yes	**
Is flow measurement provided for the flow onto the filter or the recirculated effluent if recirculation is used?	yes	**
Are the efficiencies in conformance with the NRC formulas given on pages 166 and 167 in the ASCE Sewage Treatment Plant Design Manual?	yes	**
If the filter is a single-stage high rate, does it fall into one of the types listed on pages 168 and 169 of the Design Manual?	yes	**
Does it meet the requirements listed for each type?	yes	**

*Reference numbers refer to numbers of Sections and Paragraphs of "Ten State Standards" 1968 Edition.

**References taken from the ASCE Sewage Treatment Plant Design Manual.

TABLE 2

CLASSIFICATION OF TRICKLING FILTERS

	Low Rate or "Standard" TF	High Rate TF
Hydraulic Loading		
million gallons/acre/day	1.1-4.4	8.7-44.0
gallons per day/square ft.	25-100	200-1000
Organic Loading		
lbs. BOD_5/acre-ft./day	220-1,100	1,100-13,000
lbs. BOD_5/1000 cu.ft./day	5-25	25-300
Recirculation	Never	Usually
Depth	5-10' ave. 7'	3-7' ave. 5'

1 First, calculate the organic load to be applied to the filter per day.

BOD_5 in Raw Waste = 200 ppm

BOD_5 in filter influent = (200) (1.0-0.3) = 140 ppm

$$\text{Organic Load} = (140\ \text{ppm})\left(\frac{8.34\ \text{lbs.}}{\text{gallon}}\right)(10\ \text{mgd})\left(\frac{\text{lbs./million lbs.}}{\text{ppm}}\right)$$

= 12,000 lbs. BOD_5 per day

2 Determine the design organic loading based upon the quality of the filter effluent after sedimentation required for discharge. From TABLE 2, assume a design organic load for a low rate filter of 15 lbs. BOD_5 per 1000 cubic feet per day. From FIGURE 1, the percent of BOD_5 remaining in the effluent at this loading after passing through the filter and final sedimentation would be 17 percent (83% removal). The BOD_5 concentration remaining in the plant effluent after primary and secondary treatment would be equal to,

= (200 ppm) (1.0-0.3) (1.00-0.83)

= 23.8 ppm

Let us assume this is acceptable for design purposes.

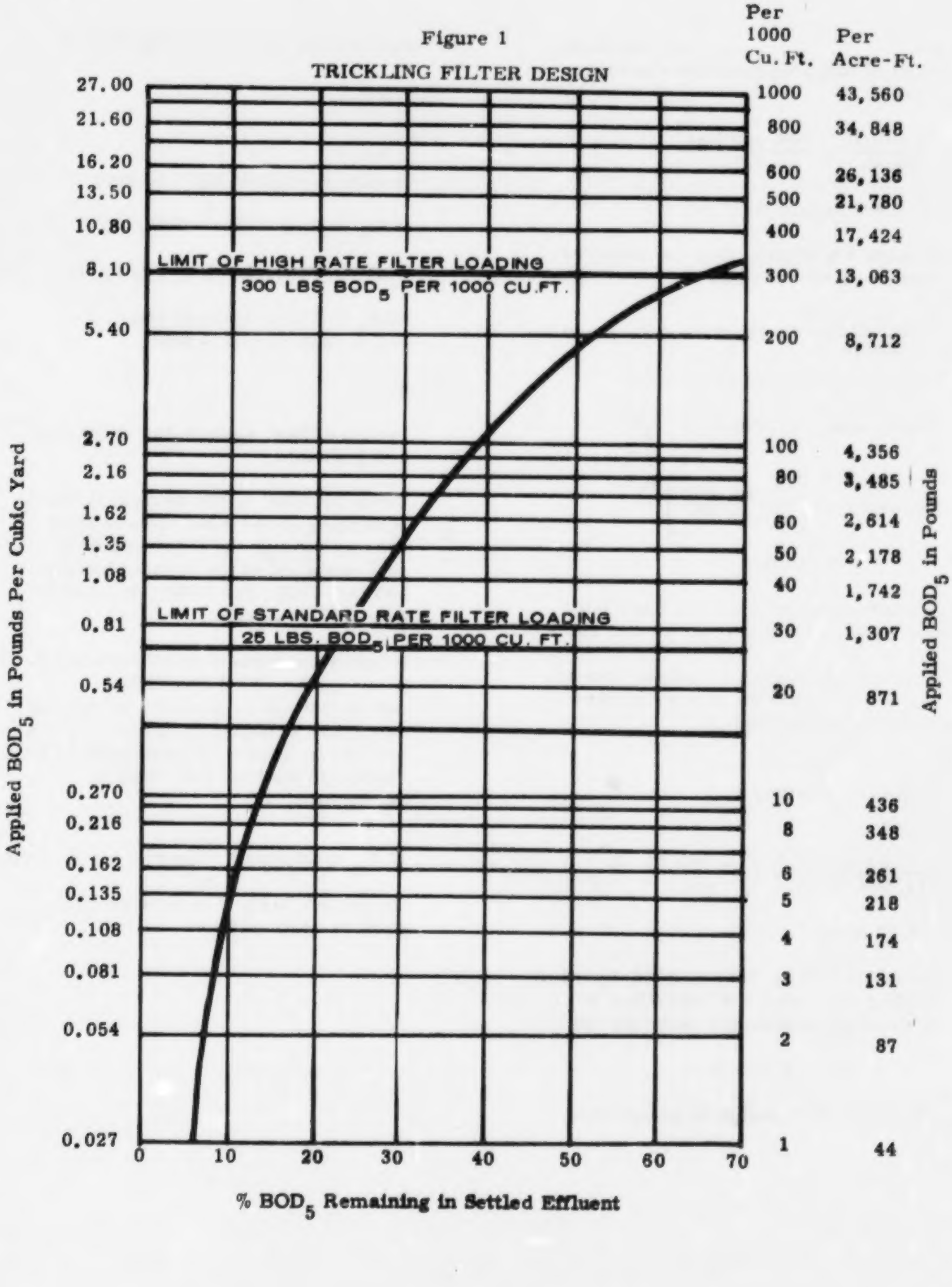
3 The required filter volume (V) is then equal to,

$$V = \frac{12{,}000\ \text{lbs. } BOD_5 \text{ per day}}{15\ \text{lbs. } BOD_5 \text{ per day/1000 cu. ft. of filter}}$$

V = 800,000 cubic feet of filter media required

Figure 1

TRICKLING FILTER DESIGN



4 Assume the filters will be 7 feet deep, then the required total filter area is equal to,

$$A = \frac{\text{Volume}}{\text{Depth}} = \frac{800,000 \text{ feet}^3}{7 \text{ ft.}}$$

$= 114,300$ square ft.

5 Provide six filters, then the required area per filter is equal to,

$$A = \frac{114,300 \text{ ft.}^2}{6 \text{ filters}} = 19,050 \text{ sq. ft. per filter}$$

6 Filter bed diameter (Diameter)

$$\text{Filter area} = 19,050 \text{ ft}^2 = \frac{\pi D^2}{4}$$

$$\text{Diameter} = \left[\frac{(4)(19,050)}{(3,1416)}\right]^{0.5}$$

$= 156$ feet

NOTE: The maximum practical filter bed diameter for construction is limited to 200 feet.

7 Checking the hydraulic loading rate to see if it is below the maximum permissible design limit.

Hydraulic Loading =

$$\left(\frac{10 \text{ mgd}}{114,300 \text{ sq. ft.}}\right)\left(\frac{43,560 \text{ sq. ft.}}{\text{acre}}\right)$$

$= 3.82$ mgad

From TABLE 2, the maximum hydraulic loading rate for a low rate filter is 4.4 million gallons per acre per day.

$(1.1 < 3.82 < 4.4)$

Therefore this design is acceptable.

B Design of High Rate Trickling Filters

Example 2

Given:

Sewage Flow Rate (Q) = 10 mgd

BOD_5 in Raw Waste = 200 ppm

BOD_5 in Filter Influent = 140 ppm

BOD_5 in Filter Effluent after sedimentation = 23.8 ppm

Problem:

Design a filter system and check for acceptability.

1 From FIGURE 1, the percent of BOD_5 remaining in the plant effluent after passing through the filter and final sedimentation at the organic loading of 100 lbs. BOD_5 per 1000 cubic feet is 40% (60% removal).

In order to produce an effluent of the same quality (23.8 ppm BOD_5 concentration) as provided by the low rate filter designed in Example 1, the maximum organic concentration to be applied to the high rate filter is determined.

$$BOD_5 \text{ maximum} = \frac{23.8 \text{ ppm}}{0.40} = 59.5 \text{ ppm}$$

As $(59.5 < 140)$, it is necessary to provide recirculation.

2 To calculate the required volume of recirculation, balance the organic load applied to the filter using the following expression -

$$(10\text{ mgd})\left(\frac{8.34\text{ lbs.}}{\text{gal.}}\right)(140\text{ ppm})\left(\frac{\text{lbs./million lbs.}}{\text{ppm}}\right)$$

$$+ (X\text{mgd})\left(\frac{8.34\text{ lbs.}}{\text{gal.}}\right)(23.8\text{ ppm})\left(\frac{\text{lbs./million lbs.}}{\text{ppm}}\right) =$$

$$(10\text{ mgd} + X\text{ mgd})\left(\frac{8.34\text{ lbs.}}{\text{gal.}}\right)(59.5\text{ ppm})\left(\frac{\text{lbs./million lbs.}}{\text{ppm}}\right)$$

Solving for X, which is the volume of recirculation required,

$$(10)(\cancel{8.34})(140) + (X)(\cancel{8.34})(23.8) = (10 + X)(\cancel{8.34})(59.5)$$

$$(1400) + (23.8)(X) = (595) + (59.5)(X)$$

$$(59.5 - 23.8)(X) = (1400 - 595)$$

$$35.7(X) = 805$$

$$X = 805/35.7 = 22.6$$

Volume of Recirculation = 22.6 mgd

3 Calculate the actual organic load to be applied to the filter. It is not equal to 12,000 lbs. BOD_5/day but,

$$\text{Organic Load} = (59.5\text{ ppm})\left(\frac{8.34\text{ lbs.}}{\text{gal.}}\right)\left(\frac{\text{lbs./million lbs.}}{\text{ppm}}\right)(10\text{ mgd} + 22.6\text{ mgd})$$

$$= (59.5)(8.34)(32.6) = 16,180\text{ lbs. } BOD_5/\text{day}$$

4 Calculate the required filter volume

$$V = \frac{16,180\text{ lbs. } BOD_5/\text{day}}{100\text{ lbs. } BOD_5/1000\text{ cu. ft./day}}$$

V = 161,800 cubic feet of filter media

5 From TABLE 2, assume a filter depth of 5 feet,

Required filter area (A) is then equal to

$$A = \frac{\text{Volume}}{\text{Depth}} = \frac{161,800\text{ cu. ft.}}{5\text{ feet}} = 32,360\text{ sq. ft.}$$

6 Filter Diameter (Diam.)

Required Filter Area = 32,360 sq.

Provide (4) filters, then the required area per filter is equal to

$$\frac{32{,}360 \text{ sq.ft.}}{4 \text{ filters}} = 8{,}090 \text{ sq.ft. per filter}$$

$$\begin{matrix}\text{Filter area} \\ 8{,}090 \text{ sq.ft.}\end{matrix} = \left[\frac{\pi D^2}{4}\right]$$

$$\text{Diam.} = \left[\frac{(4)\ (8{,}090)}{\pi}\right]^{0.5} = (10{,}300)^{0.5}$$

Diam. = 101.5 feet

7 From TABLE 2, the maximum hydraulic loading for a high - rate filter is 44 million gallons per acre per day.

Checking the hydraulic loading rate to see if it falls below this maximum design limit,

$$\begin{matrix}\text{Hydraulic Loading} \\ \text{Rate (mgad)}\end{matrix} = \left(\frac{10 \text{ mgd} + 22.6 \text{ mgd}}{32{,}360 \text{ sq. ft.}}\right) \left(\frac{43{,}560 \text{ sq.ft.}}{\text{acre}}\right)$$

$$= \left(\frac{32.6}{32{,}360}\right) \left(\frac{43{,}560}{1}\right)$$

$$= 44 \text{ mgad}$$

$$(44 \leq 44)$$

Therefore this design is acceptable.

IV NATIONAL RESEARCH COUNCIL FORMULA

The National Research Council (NRC) formula for calculation of trickling filter efficiency was developed from military wastewater treatment plant operational data collected during World War II. These formulas are based upon the overall 5-day Biochemical Oxygen Demand (BOD_5) removal achieved through trickling filtration plus subsequent final settling.

A Single Stage Trickling Filter Design

1 The basic NRC formula for the design of single-stage trickling filters is:

$$E = \frac{1}{\left[1 + C \quad \left(\frac{W}{VF}\right)\right]^{0.5}}$$

where,

E = the fraction of BOD_5 removed in the first stage filter

W = the organic load influent to the filter in pounds per day (lbs/day of BOD_5)

$W = (8.34)\ Q\ L_1$

V = the filter volume in 1,000 cu. ft.

F = the recirculation factor

$$F = \frac{1 + R}{[1 + (1 - p)\ R]^2}$$

P = fraction of BOD_5 available ($0.85 < P < 0.95$),

generally use $P = 0.90$

$C = 0.0561$

Q = the flow rate in mgd

L_1 = the influent BOD_5 concentration in mg/l or ppm

R = the recirculation ratio, or the ratio of recirculation flow to the total plant influent flow

2 Rearranging terms to solve for the volume of rock media required in the first stage filter, the NRC formula becomes:

$$V = (0.0263)\ QL_1 \frac{[1 + (0.1)\ (R)]^2}{1 + R} \left(\frac{E}{1 - E}\right)^2$$

3 Example 3 - Single Stage Trickling Filter Design

Given: Sewage Flow Rate = 10 MGD

BOD_5 of effluent = 24 ppm

BOD_5 of influent = 140 ppm

R = 1.0

Find: Required filter volume (V)

a The fraction of BOD_5 to be removed by the filter (E) is equal to

$$E = \left(\frac{140 - 24}{140}\right) = 0.83$$

b Solving for the required filter volume (V) using the basic NRC formula,

$$V = (0.0263)\ Q\ L_i\ \frac{[1 + (0.1)(R)]^2}{(1 + R)}\ \left(\frac{E}{1 - E}\right)^2$$

$$V = (0.0263)\ (10\ \text{MGD})\ (140)\ \frac{(1.1)^2}{2}\ \left(\frac{0.83}{0.17}\right)^2$$

$$= (0.0263\ (10)\ (140)\ (0.605)\ (24.3)$$

$$= 542$$

The required filter volume is therefore equal to 542,000 cubic feet.

B Two Stage Trickling Filter Design

1 For second stage filters, a decrease in waste treatability is provided in the NRC formula proportional to the amount of BOD removed in the first stage filter and equal to the term

$$\left[\frac{1}{1 - E_1}\right]^2$$

in which E_1 is the efficiency of the first stage. The efficiency of the second stage (E_2) is equal to

$$E_2 = \frac{1}{1 + 0.0561\left(\frac{W_2}{VF\ (1 - E_1)^2}\right)^{0.5}}$$

where,

W_2 = the organic load to be applied to the second stage filter

$W_2 = W_1\ (1 - E_1)$

W_1 = the organic load applied to the first stage filter

2 The NRC formula for second-stage filters with terms rearranged to solve for the required filter volume becomes,

$$V = (0.0263)\ Q\ L_i\ \frac{[1 + (0.1)(R_2)]^2}{1 + R_2}\ \left[\frac{E_2}{(1 - E_1)(1 - E_2)}\right]^2$$

where,

R_2 = recirculation ratio for the second-stage filter

E_1 = the efficiency of the first stage filter

E_2 = the efficiency of the second filter

$$E_2 = \left[\frac{1}{1 - E_1}\right]^2$$

3 Example 4 - Two Stage Trickling Filter Design

Given: Sewage Flow Rate = 10 MGD

BOD_5 of effluent (L_e) = 24 ppm

BOD_5 of influent (L_i) = 140 ppm

E_1 = 0.6 or 60% BOD_5 removal

R_1 = 1.0

R_2 = 1.0

Find:

Required first-stage filter volume (V_1)

Required second-stage filter volume (V_2)

Total required filter volume
$(V) = (V_1 - V_2)$

a The required filter volume of the first-stage filter (V_1) is equal to,

$$V_1 = (0.0263)\ Q\ L_i\ \frac{[1 + (0.1)\ R_1]^2}{(1 + R_1)}\left(\frac{E_1}{1 - E_1}\right)^2$$

$$= (0.0263)\ (10)\ (140)\ \frac{[1 + (0.1)\ (1)]^2}{(1 + 1)}\left(\frac{0.6}{1 - 0.6}\right)^2$$

$$= (0.0263)\ (10)\ (140)\ (0.605)\ (2.25)$$

$$= 50$$

V_1 is therefore equal to 50,000 cubic feet.

b The required filter volume of the second-stage filter (V_2) is equal to,

$$V_2 = (0.0263)\ Q\ L_i\ \frac{[1 + (0.1)\ (R_2)]^2}{(1 + R_2)}$$

$$\left[\frac{E_2}{(1 - E_1)\ (1 - E_2)}\right]^2$$

where

L_i = the BOD_5 of the influent applied to the second stage filter

R_2 = the recirculation ratio for the second stage filter

Solving first for the value of E_2,

$$E_2 = 1 - \left(\frac{1 - E}{1 - E_1}\right) = 1 - \left(\frac{1 - 0.9}{1 - 0.6}\right) = 0.75$$

Next, determine the BOD_5 content of the influent applied to the second stage filter.

$$L_i = (140\ mg/l)\ (1 - 0.6) = 56\ mg/l$$

Then, for $R_2 = 1.0$

$$V_2 = (0.0263)\ (10)\ (56)\ \frac{(1 + 0.1)^2}{1 + 1}$$

$$\left[\frac{0.75}{(1 - 0.6)\ (1 - 0.75)}\right]^2$$

$$= (0.0263)\ (10)\ (56)\ (0.605)\ (56.25)$$

$$= 497$$

V_2 is therefore equal to 497,000 cubic feet.

c The total filter volume (V) is equal to,

$$V = (V_1 + V_2)$$

$$= (50,000 + 497,000)$$

$$= 547,000 \text{ cubic feet}$$

V ECKENFELDER FORMULA

The basic Eckenfelder Formula for treatment of sewage and industrial wastes by BOD_5 removal is:

$$\frac{Le}{Lo} = \frac{1}{1 + \frac{CD^{0.67}}{(QA)^{0.5}}}$$

where

Le = the BOD_5 concentration remaining in the filter effluent, in mg/l

Lo = the BOD_5 concentration actually applied to the filter, including influent flow plus recirculation

Q = sewage flow rate in mgd

A = filter area in acres

D = depth of filter in feet

C = 2.5

Eckenfelder defined the influence of recirculation on waste treatment with the following expression:

$$Lo = \frac{Li + R\ Le}{1 + R} \quad \text{in which,}$$

Lo = the mg/l of BOD_5 actually applied to the filter

Le = the mg/l of BOD_5 in the filter effluent

Li = the mg/l of BOD_5 contained in the settled raw sewage waste

R = the recirculation ratio

A Single-Stage Trickling Filter Design

1 Rearranging terms to solve for the volume of rock required, the Eckenfelder formula for the design of single stage trickling filters becomes:

$$V = (7.0)\ \frac{Q}{D^{0.33}} \left[\frac{E}{(1 - E)\ (1 + R)}\right]^2$$

where,

V = filter volume in 1000 cubic feet

Q = sewage flow rate in mgd

D = filter depth in feet

E = the fraction of BOD_5 removed, or the efficiency of the filter stage

R = the recirculation ratio

2 Example 5 - Single Stage Trickling Filter Design using the Eckenfelder Formula

Given: Sewage Flow Rate = 10 MGD

BOD_5 of effluent (Le) = 24 ppm

BOD_5 of influent (Li) = 140 ppm

R = 1.0

T = 20° C

D = 7.0 feet

Find: Required filter volume (V)

a Filter efficiency (E) is equal to,

$$E = \left(\frac{Li - Le}{Li}\right) = \left(\frac{140 - 24}{140}\right) = 0.83$$

b The required filter volume (V) is equal to,

$$V = 7\frac{Q}{D^{0.33}} \left[\frac{E}{(1 - E)\ (1 + R)}\right]^2$$

For R = 1 and D = 7 ft.,

$$V = \frac{(7)\ (10)}{(7)^{0.33}} \left[\frac{(0.83)}{(1 - 0.83)\ (1 + 1)}\right]^2$$

$$= \frac{(7)\ (10)\ \ (0.689)}{(1.915)\ \ (0.1157)}$$

$$V = \left(\frac{48.2}{0.22}\right) = 218, \text{ or } 218,000 \text{ cubic feet}$$

B Two-Stage Trickling Filter Design

1 The Eckenfelder Formula for the design of two-stage trickling filters becomes,

$$V = \frac{7\ Q}{D^{0.33}} \left[\frac{E_2}{(1 - E_1)\ (1 - E_2)\ (1 + R)}\right]^2$$

where $E_2 = \left[1 - \frac{(1 - E)}{(1 - E_1)}\right]$

2 Example 6 - Design of Two-Stage Trickling Filter using the Eckenfelder Formula

Given: Sewage Flow Rate (Q) = 10 MGD

BOD_5 of effluent (Le) = 24 ppm

BOD_5 of influent (Li) = 140 ppm

$E_1 = 0.6$ or 60%

$R_1 = 1.0$

$R_2 = 1.0$

$D = 7.0$ ft.

$T = 20^\circ C$

Find:

Required First-Stage Filter Volume (V_1)

Required Second-Stage Filter Volume (V_2)

Total required filter volume (V) = ($V_1 + V_2$)

a First-Stage Filter Volume (V_1)

$$V_1 = \frac{7\ Q}{D^{0.33}} \left[\frac{E_1}{(1 - E_1)(1 + R)}\right]^2$$

$$= \frac{(7)(10)}{(7)^{0.33}} \left[\frac{(0.6)}{(1 - 0.6)\ (1 + 1)}\right]^2$$

$$= \frac{(7)(10)\ (0.36)}{(1.915)(0.64)} = 20.6$$

The required first-stage filter volume (V_1) is therefore equal to 20,600 cubic feet.

b Second-Stage Filter Volume (V_2)

$$E_2 = \left[1 - \frac{(1 - E)}{(1 - E_1)}\right] = \left[1 - \frac{(1 - 0.83)}{(1 - 0.6)}\right]$$

$$= \left[1 - \left(\frac{0.17}{0.4}\right)\right] = (1 - 0.425)$$

$$E_2 = 0.575$$

$$V_2 = \frac{7\ Q}{D^{0.33}} \left[\frac{E_2}{(1 - E_1)(1 - E_2)(1 + R_2)}\right]^2$$

$$= \frac{(7)(10)}{(7)^{0.33}} \left[\frac{(0.575)}{(1 - 0.6)(1 - 0.575)(1 + 1)}\right]^2$$

$$= \frac{(7)(10)(0.33)}{(1.915)(0.1155)} = 104.8$$

The required second-stage filter volume is therefore equal to 104,800 cubic feet.

c The total required filter volume (V) is equal to,

$V = (V_1 + V_2)$

= (20,600 + 104,800)

= 125,400 cubic feet

VI GALLER - GOTAAS FORMULA

Design charts derived from the Galler-Gotaas formulations for biological waste treatment-design are provided in this section of the outline. These charts are based upon the following formula which was developed from a multiple regression analysis of operational data from existing sewage treatment plants:

$$Le = \frac{(0.464)\,(Lo)^{1.19}(1 + R)^{0.28}(Q/A)^{0.13}}{(1 + D)^{0.67}(T)^{0.15}}$$

where,

Lo = the concentration of BOD_5 in the combined influent (recirculation plus raw settled sewage) to be applied to the filter.

Le = the concentration of BOD_5 of the effluent from the filter in mg/l.

R = the recirculation ratio or the ratio of recirculation flow to plant influent flow.

Q = the sewage flow rate in million gallons per day (mgd).

A = filter area, in square feet.

D = depth of filter in feet.

T = the temperature of the wastewater in degrees centigrade.

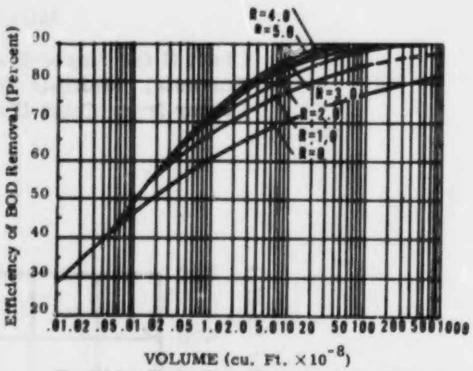
A Single Stage Trickling Filter Design

1 Rearranging terms to solve for the volume of rock required, the Galler-Gotaas formula for the design of single stage trickling filters becomes--

$$V = (0.1355)\,(D)\;\frac{(Q)^{0.13}(Li)^{0.19}\;[1 + R\,(1 - E)]^{1.19}}{(T)^{0.15}(1 + D)^{0.67}\,(1 - E)\,(1 + R)^{0.78}}$$

2 Figures 2, 3, 4 and 5 have been developed from the above equation. These graphs may be used to design a single-stage or first-stage trickling filter.

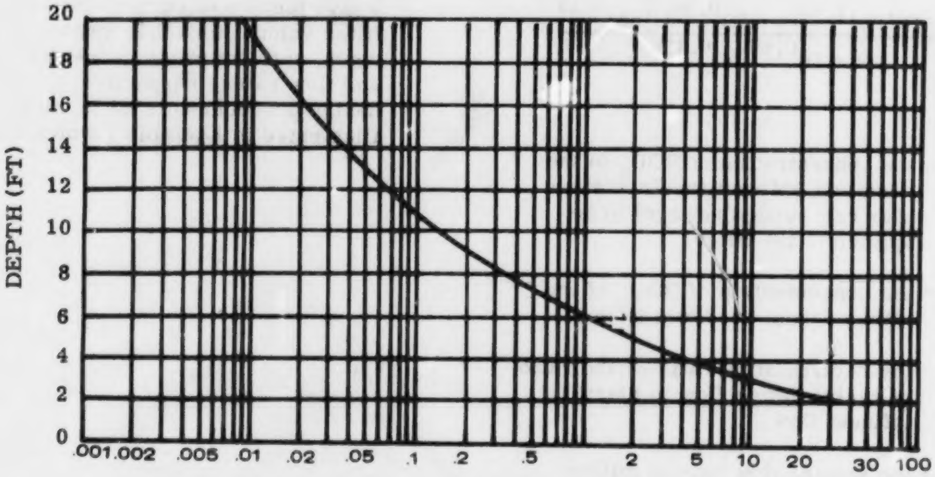
Figure 2 is for the design of a single-stage trickling filter with an influent flow rate of 1.0 mgd, an influent BOD_5 waste concentration of 100 mg/l, filter depth of 6.0 feet, and a wastewater temperature of 20° C. Figures 3, 4 and 5 give factors to correct the required filter volume for other values of filter depth, influent waste concentrations and flow rates, respectively. The design procedures to be followed are illustrated in Example 7 which follows:



8

Chart I for Single-Stage Trickling Filter Design by Galler-Gotaas Formula. Constructed on the Base of L_1 - 100 mg/l, Q - 1.0 mgd, D = 6.0 ft., and T = 20° C.

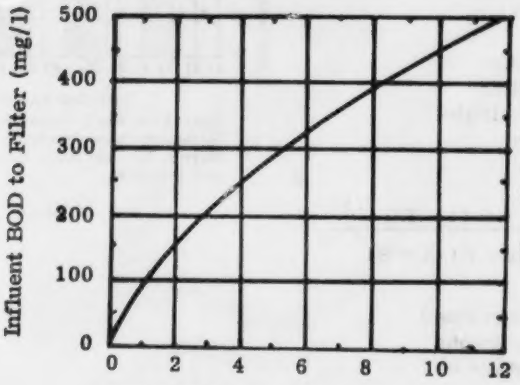
Figure 2



MULTIPLICATION FACTOR

Chart II for Single-Stage Trickling Filter Design by Galler-Gotaas Formula. Multiply Volume Determined from Chart I by Appropriate Factor from Chart II for Filter Depths other than 6 ft.

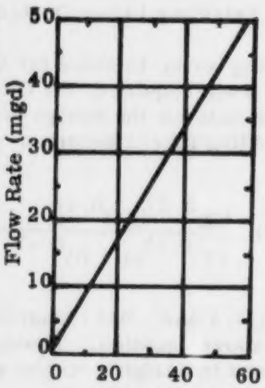
Figure 3



MULTIPLICATION FACTOR

Chart III for Single-Stage Trickling Filter Design by Galler-Gotaas Formula. Multiply Volume Determined from Chart I by Appropriate Factor from Chart III for Influent BOD concentrations other than 100 mg/1

Figure 4



Multiplication Factor

Chart IV for Single-Stage Trickling Filter Design by Galler-Gotaas Formula. Multiply Volume determined from Chart I by appropriate factor from Chart IV for Plant Flow Rates Other than 1.0 mgd.

Figure 5

3 Example 7 - Single-Stage Trickling Filter Design using the Modified Galler-Gotaas Formula

Given: Sewage Flow Rate = 10 MGD

BOD_5 of effluent (Le) = 24 ppm

BOD_5 of influent (Li) = 140 ppm

R = 1.0

Find: Required filter volume (V)

a The fraction of BOD_5 to be removed by the filter (E), or the required efficiency of the filter is equal to,

$$E = \frac{Li - Le}{Li} = \frac{140 - 24}{140} = 0.83 \text{ or } 83\%$$

b Assume that the wastewater temperature is 20°C. If it is not, the required filter volume must be corrected by the factor

$$\frac{20}{T}^{0.15}$$

c From Figure 2, with a recirculation ratio (R) equal to 1.0, the required filter volume (V) is equal to 60,000 cubic feet. Assume a filter depth (D) of 7 feet. From Figure 3, the multiplication factor to correct the filter volume for this depth is equal to 0.6.

From Figure 4, the multiplication factor to correct the filter volume for the influent BOD_5 concentration of 140 ppm is equal to 1.6.

From Figure 5, the multiplication factor to correct the filter volume for the sewage flow rate of 10 MGD is equal to 11.0. The corrected filter volume required (V) is then equal to,

$$V = (60,000)(0.6)(1.6)(11)$$

$$= 633,000 \text{ cubic feet}$$

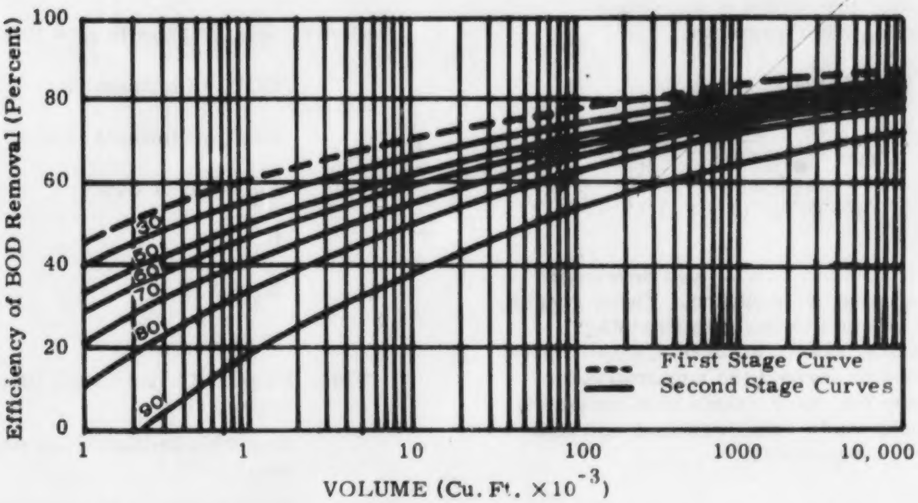


Chart I for Two-Stage Trickling Filter Design by the Galler-Gotaas Formula. Constructed on the Base of L_i = 100 mg/l, Q = 1.0 mgd, R = 0.0, D = 6.0 ft., and T = 20°C.

Figure 6

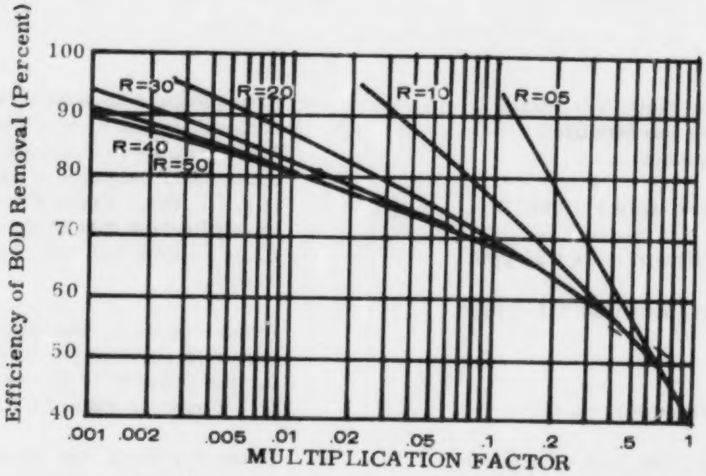


Chart II for Two-Stage Trickling Filter Design by Galler-Gotaas Formula. Multiply Volume from Chart I by Appropriate Factor for Filters with Recirculation.

Figure 7

B Two-Stage Trickling Filter Design

1 Rearranging terms to solve for the volume of filter rock required and introducing the term $[1/(1 - E_1)]^4$ to correct for reduced waste treatability, results in the following equation for design of two-stage trickling filter systems:

$$V = (0.1355)(D)\left[\frac{(Q)^{0.13}(Li)^{0.19}(1 + R)(1 - E_2)^{1.19}}{(T)^{0.15}(1 + D)^{0.67}(1 - E_2)(1 + R)^{0.78}(1 - E_1)^{0.5}}\right]$$

2 Figures 6 and 7 have been developed from the above equation. These graphs may be used to design a two-stage trickling filter. Figures 3, 4 and 5 give factors to correct the required filter volume for other values of filter depth, influent waste concentrations and flow rates, respectively.

The design procedures to be followed are illustrated in Example 8 which follows:

3 Example 8 - Two Stage Trickling Filter Design using the Modified Galler - Gotaas Formula

Given: Sewage Flow Rate = 10 MGD

BOD_5 of effluent (Le) = 24 ppm

BOD_5 of influent (Li) = 140 ppm

$E_1 = 0.6$ or 60%

$R_1 = 1.0$

$R_2 = 1.0$

$T = 20°C$

Find: Required First-Stage filter volume (V_1)

Required Second-Stage filter volume (V_2)

Total required filter volume $(V) = (V_1 + V_2)$

a From Figure 6, with a first-stage filter BOD_5 removal efficiency equal to 60%, the required filter volume is 1,200 cubic feet.

From Figure 7, with a recirculation ratio (R_1) equal to 1.0, the multiplication factor to correct the filter volume for a recirculation ratio of this value is equal to 3.3. Assume a first-stage filter depth equal to 7.0 feet. From Figure 3, the multiplication factor to correct the filter volume for this depth is equal to 0.6.

From Figure 4, the multiplication factor to correct the filter volume for the influent BOD_5 concentration of 140 ppm is equal to 1.6.

From Figure 5, the multiplication factor to correct the filter volume for the sewage flow rate of 10 MGD is equal to 11.0. The corrected first-stage filter volume (V_1) is then equal to,

$$V_1 = (1,200)(3.3)(0.6)(1.6)(11.0)$$

$$= 41,800 \text{ cubic feet}$$

b The required second-stage BOD_5 removal efficiency (E_2) is equal to,

$$E_2 = \left[1 - \frac{(1 - E)}{(1 - E_1)}\right]$$

$$= \left[1 - \frac{(1 - 0.83)}{(1 - 0.6)}\right] = \left[1 - \frac{0.17}{0.40}\right]$$

$$= (1 - 0.425)$$

$$= 0.575$$

c From Figure 6, the required second-stage filter volume is equal to 5,000 cubic feet.

From Figure 7, with a recirculation ratio (R_2) equal to 1.0, the multiplication factor to correct the filter volume for a recirculation ratio of this value is equal to 4.1. Assume a second-stage filter depth equal to 7.0 feet. From Figure 3, the multiplication factor to correct the filter volume for this depth is equal to 0.6.

From Figure 4, the multiplication factor to correct the filter volume for the influent BOD_5 concentration of 56 ppm or [140 ppm × (1 - 0.6)] is equal to 0.5.

From Figure 5, the multiplication factor to correct the filter volume for the sewage flow rate of 10 MGD is equal to 11.0. The corrected second-stage filter volume (V_2) is then equal to,

$$V_2 = (5,000)(4.1)(0.6)(0.5)(11.0)$$

$$= 67,600 \text{ cubic feet}$$

d The total required filter volume (V) is then equal to,

$$V = (V_1 + V_2)$$

$$= (41,800 + 67,600)$$

$$= 109,400 \text{ cubic feet}$$

ACKNOWLEDGEMENT:

Portions of this outline were taken from a previous outline prepared by Quintin B. Graves, Professor of Civil Engineering, School of Civil Engineering, Oklahoma State University, Stillwater.

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STATUS OF OXIDATION POND PROCESSES

I DEFINITION

The term "Oxidation Pond" or "Waste Pond" may be applied to any quiescent body of water into which wastes are intentionally introduced. The terms, however, are usually reserved for impoundments of waste water which are created by construction of earthwork embankments and excavations or combinations thereof into which wastes are conveyed by pressure conduits, gravity sewers, or open canals.

II POND TERMINOLOGY AND APPLICATIONS

A Applied terms tend to be associated with applications; terminology is loose, often misapplied, and subject to change according to performance and neighborhood response. Lack of understanding, vagaries of the situation, changes in loading, or neglect contribute to the situation. Ponds are common where land costs are lower. Low operational costs are attractive, but the essentials must not be neglected; resulting unfortunate developments lead to derisive terms that tend to be remembered. The following discussion includes some of the items contributing to terms and applications.

B The relationships between dissolved molecular oxygen and microbial activity provide a logical basis for pond classification.

1 Aerobic - contains dissolved molecular oxygen thruout the water mass at all times.

2 Anaerobic - Designed and operated for use in the absence of detectable molecular oxygen in the water mass.

3 Facultative - The most common type of pond is characterized by a dissolved oxygen excess in upper layers of water and a molecular oxygen deficiency in lower layers of the pond.

C Overflow characteristics provide another basis of terminology according to usage:

1 Terminal ponds have no surface overflow. The terminal pond may be further classified as percolating when the water loss mainly occurs by movement into the substrata or evaporative if that happens to be the main reason for prevention of out flow. Both are usually involved.

2 Overflowing or detention ponds have an inlet and outlet with some form of basin between.

3 Intermittent ponds may have a surface overflow during wet weather or high inflow rates,with no overflow at other times.

D Common terminology may be associated with inflow characteristics or sources such as:

1 Sewage ponds or lagoons
2 Feed lot or agricultural drainage
3 Canning, paper mill, meat packing or other industrial drainage ponds.

E Ponds may be classified according to their stage of use in an integrated treatment system.

1 An equilization pond may be used to smooth the flow for subsequent operations.

2 A settling pond may be used to decrease gross solids discharges into other operations and/or to decrease organic loading.

3 The pond may follow primary, secondary or advanced treatment. A polishing pond may be used to back up any treatment operation to improve regular operation or decrease effects of contingencies.

4 A series of ponds may be designated in terms of relative member in the series, such as primary, secondary, tertiary, quaternary, etc.

5 The pond may be used for holding organic sludge, storm water, silt or process sludges, and named accordingly. The pond may be a terminal disposal site to be abandoned when filled, or an holding pond subject to subsequent reprocessing and takeout.

F Loading rate may be the basis of another system of terminology:

1 A high-rate pond may have a high rate of input relative to volume.

2 Low-rate ponds usually have low volumetric, or organic loading relative to volume capacity or time.

3 Intermediate rates may be anything between.

4 The rate concept may be based upon detention time, volume, area, depth, organic content, food/microorganism ratios, solids content, etc.

G The predominant microbiologied activity occurring, or of interest, provides a basis for pond classification:

1 A stabilization pond covers almost any pond class involving mixed growth, detention time and degrees of treatment.

2 An algal pond includes those in which algae can and do grow. This usually means a detention time of 3 or more days and conditions suitable for growth. A long detention time may permit deposition and clarification. Dispersed growth in the outflow characterizes intermediate detention times.

3 A reduction or treatment pond may be characterized by high activities of reducer organisms, such as bacteria fungi or slime organisms. Growth or circulation may lead to diminished light penetration limiting algal activity. These may be considered contact, holding, or high rate ponds. They may be predominantly anaerobic or aerated to maintain circulation and molecular oxygen content. If sludge is returned, or liquid recycled, a new terminology opens.

H Ponds may be associated with one or more large variety of purposes that lead to applied terms:

1 If it is associated with open space, green belt, or community planning, the actual use may change terminology drastically.

2 Wild life propagation, wet lands, marsh development are another basis for terms and use.

3 Ponds may be used for water, land, nutrient, energy recycle, or as a barrier for salt water intrusion. Since ponds eventually fill, land reclamation for park, residential or industrial activities may become progressive uses with water renovation and recharge during early events.

4 Industrial ponds may be used for cooling, recycle water, fire protection, surface irrigation, solids reclamation, pumped storage, or treatment of source or wastewaters. Retention and control of storm water may be intended.

III FUNCTIONAL MECHANISMS AND DESIGN

Waste component stabilization, solids disposal and liquid retention are fundamental considerations in pond design and use.

A Rigorous evaluation of the hydraulic regime including inflow, outflow, percolation and evaporation are first considerations in capacity requirements.

1 The general relationship for ponds (or other wastewater treatment) is:

$$\mu A = Q \qquad (1)$$

where μ is a loading or dissipation velocity

Q is the volume of liquid entering or leaving the pond.

A is pond area

2 The instantaneous velocity of all water entering a pond is $\mu_{in} + i + P_i$

where $\mu_{in} = Q_{in}/A$

i = the rate of precipitation (rainfall)

P_i = rate of groundwater infiltration.

3 The instantaneous velocity of water leaving the pond is $\mu_{out} + P_o + E$

where: $\mu_{out} = Q_{out}/A$

P_o = the rate of exfiltration or percolation

E = the evaporation rate

4 The hydraulic balance for any pond at any instant is:

$$\mu_{in} + i + P_i = \mu_{out} + P_o + E \qquad (2)$$

or regrouped:

$$\mu_{in} - \mu_o = (E-i) + (P_o - P_i) \qquad (3)$$

5 The volume of water leaving the pond by overflow is a major concern because of its influence on the receiving water.

$$\mu_{out} = \mu_{in} - [\,(E-i) + (P_o - P_i)]$$

a For an overflowing pond:

$$\mu_{in} > (E-i) + (P_o - P_i)$$

b For a non overflowing pond

$$\mu_{in} < (E - i) + (P_o - P_i)$$

B Non overflowing ponds

1 To have a ponding system which never has a surface overflow, it is essential to have a variable input or a variable surface area to provide for storage.

2 Net evaporation (E-i) or E_n) generally is available from long term records of precipitation and evaporation.

Evaluation of month by month data as in Table 1 gives an estimate of E_n.

a From Fig. 1 the net evaporation per year is 44.5 in. and in July reaches a maximum of 130 inches. The mean rate is 0.122 in/day.

b 0.122 in/day represents 3320 gal/A/day.

c At a per capita use of 80 gal/cap/day in the situation in Table 1, evaporation alone will dispose of the wastes of 41 persons per acre throughout the year. During July, the wastewaters of 121 persons per acre could be evaporated.

3 As indicated in Figure 1, a pond receiving water at the rate of 0.1 in./day would have to be about 38 in. deep to avoid becoming dry before the next rainy season and could increase in depth by 25 in. during the rainy season. For a minimum depth of 3 ft., as recommended, the design depth of slightly over 6 ft. is indicated by E_n data.

TABLE I

TYPICAL ANALYSIS EVAPORATION-PRECIPITATION

Month	Evap. E inches	Precip. i inches	E-i inches	(E-i) Year 1	Cumulative Year 2
Jan.	1.1	5.1	-4.0	-4.3	+40.0
Feb.	2.0	4.3	-2.3	-6.6	+37.7
Mar.	3.6	3.6	-0.0	-6.6	+37.7
Apr.	5.6	2.1	+3.5	-3.1	+41.2
May	8.2	0.5	+7.7	+4.6	+48.9
June	9.0	0.0	+9.0	+13.6	+57.0
July	10.8	0.0	+10.8	+24.4	+67.8
Aug.	9.8	0.0	+9.8	+34.2	+77.6
Sept.	7.8	0.0	+7.8	+41.0	+85.4
Oct.	5.0	0.3	+4.7	+45.7	+90.1
Nov.	2.3	1.4	+0.8	+46.5	+90.9
Dec.	1.2	4.1	-2.9	+44.0	+87.2

Figure 1 shows these data in graphic form.

Figure 1.

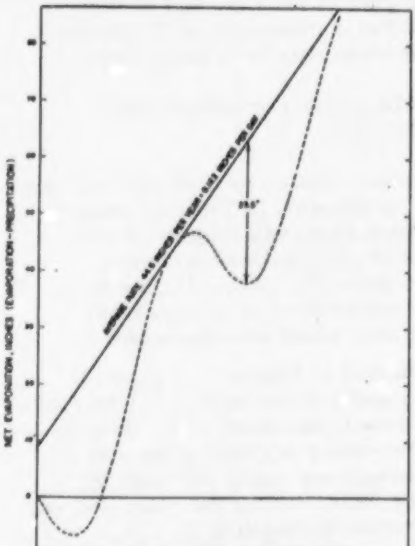


Figure 1. Net Evaporation from a Pond as a Function of Time of Year

28-4

4 Net percolation rate ($P_o - P_1$) may be estimated reasonably well on operating ponds but is difficult to estimate for design purposes.

- a If ponds are located above groundwater level, intrusion is unlikely; P_1 becomes zero and P_o or water moving toward the ground water level depends on soil permeability, pressure, area and boundary behavior. Divert storm inflow.
- b Table II includes observed percolation plus evaporation rates for a number of operating ponds in California and various soil characteristics.
- c Percolation rates may also be estimated by shutting off inflow and outflow or diversion for a 24 hour period without rainfall. The depth measurements before and after indicate percolation plus evaporation if the water level is above the groundwater table. Pan evaporation measurements simultaneously permit evaporation loss estimation (pan evaporation rates commonly are about 1.25 pond evaporation). The net percolation rate is available by difference.
- d Careful metering of inflow and outflow permit percolation rate estimates as in c without flow interruption if evaporation rate and surface levels are determined.
- e Percolation tests as described for septic tanks (1) do not extend over enough time to be of value in pond design. A test developed, used, and still under evaluation by the author for the past 10 years is outlined in Figure 2. This test is more rigorous because it includes simulation of hydraulic head, continual submergence for 14 days, bottom lining and conditions close to the actual situation. A plot of loss per day

TABLE II

NET PERCOLATION PLUS NET EVAPORATION RATES IN VARIOUS PONDS AND SOIL TYPES IN CENTRAL CALIFORNIA

POND SYSTEM	POND SIZE ACRES	POND DEPTH INCHES	SOIL TYPE	APPROXIMATE TERMINAL LOSS RATE*	
				INCHES DAY^{-1}	GALLONS ACRE^{-1} DAY^{-1}
Woodland South (Ave.)	22	60	Heavy Silty Clay	0.40	11000
American Canyon	4		Coastal Silt		
July-Aug.				0.46	12500
Feb.-Mar.				0.25	6800
Esparto	2	72	Light Silty Clay		
July-Aug.				0.66(1)	18000
Feb.-Mar.				0.25	6800
St. Helena (Ave)	19	144	Greyish Loam	0.66	18000
Woodland North (Ave.)	2	60	Alkaline Silt	0.73	20000
Woodland Pilot (Ave.)	1/4	60	Alkaline Silt	0.75	20200
Gonzales (Ave.)	3	72	Fine Sand	1.30	35000
Rio Lindo (Ave.)	1/2	72	Gravel with Silt	1.50	41000
Berryessa Resorts (Summer)	1/4	36-72	Course Shale	2.5	68000

*Includes net evaporation which may average 0.1 inch per day and equal 0.3 inch per day during summer. Percolation rates apparently decrease in winter and increase in summer and seem to be influenced by viscosity and gas production in the bottom.

(1) July-August evap. = 0.35 in per day.

(2) In Central California evaporation and precipitation are usually approximately equal in March and hence, net evaporation is 0. Therefore, March values are mainly, Percolation P_o.

may indicate the approach to long time equilibrium if conditions remain uniform. Experience has shown that data obtained from the test as in Figure 2 is valid to be used on strong sewage percolation rates on a long term basis. Comparative tests and pond performance seem to yield conservative data.

Currently available hydraulic loss rates in central California ponds (Table 2) generally approach 0.5 in + or - 0.25 inches with some exceptions. A loss rate of 0.5 inches per day represents 13600 gal/A/day or the wastewater load from 136 persons/A/day at 100 gal/cap/day water use rate.

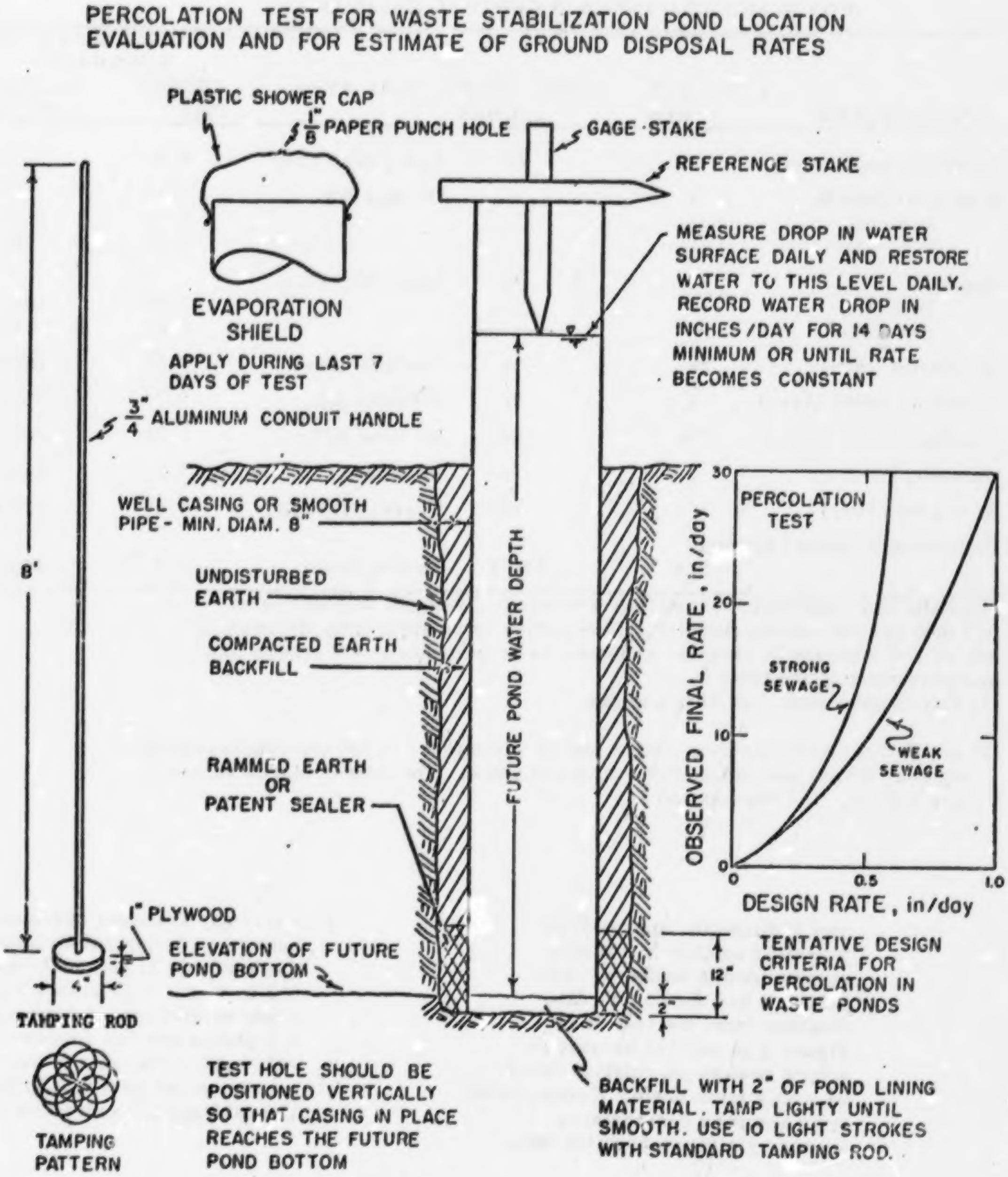

PERCOLATION TEST FOR WASTE STABILIZATION POND LOCATION EVALUATION AND FOR ESTIMATE OF GROUND DISPOSAL RATES
PLASTIC SHOWER CAP
1/8" PAPER PUNCH HOLE
GAGE STAKE
REFERENCE STAKE
EVAPORATION SHIELD
APPLY DURING LAST 7 DAYS OF TEST
MEASURE DROP IN WATER SURFACE DAILY AND RESTORE WATER TO THIS LEVEL DAILY. RECORD WATER DROP IN INCHES/DAY FOR 14 DAYS MINIMUM OR UNTIL RATE BECOMES CONSTANT
3/4" ALUMINUM CONDUIT HANDLE
8'
WELL CASING OR SMOOTH PIPE - MIN. DIAM. 8"
UNDISTURBED EARTH
COMPACTED EARTH BACKFILL
FUTURE POND WATER DEPTH
RAMMED EARTH OR PATENT SEALER
1" PLYWOOD
ELEVATION OF FUTURE POND BOTTOM
4"
1"
TAMPING ROD
12"
2"
TENTATIVE DESIGN CRITERIA FOR PERCOLATION IN WASTE PONDS
TAMPING PATTERN
TEST HOLE SHOULD BE POSITIONED VERTICALLY SO THAT CASING IN PLACE REACHES THE FUTURE POND BOTTOM
BACKFILL WITH 2" OF POND LINING MATERIAL. TAMP LIGHTY UNTIL SMOOTH. USE 10 LIGHT STROKES WITH STANDARD TAMPING ROD.
PERCOLATION TEST
OBSERVED FINAL RATE, in/day
30
20
10
0
STRONG SEWAGE
WEAK SEWAGE
0
0.5
1.0
DESIGN RATE, in/day

FIGURE 2 PERCOLATION TEST SET-UP FOR WASTE POND DESIGN

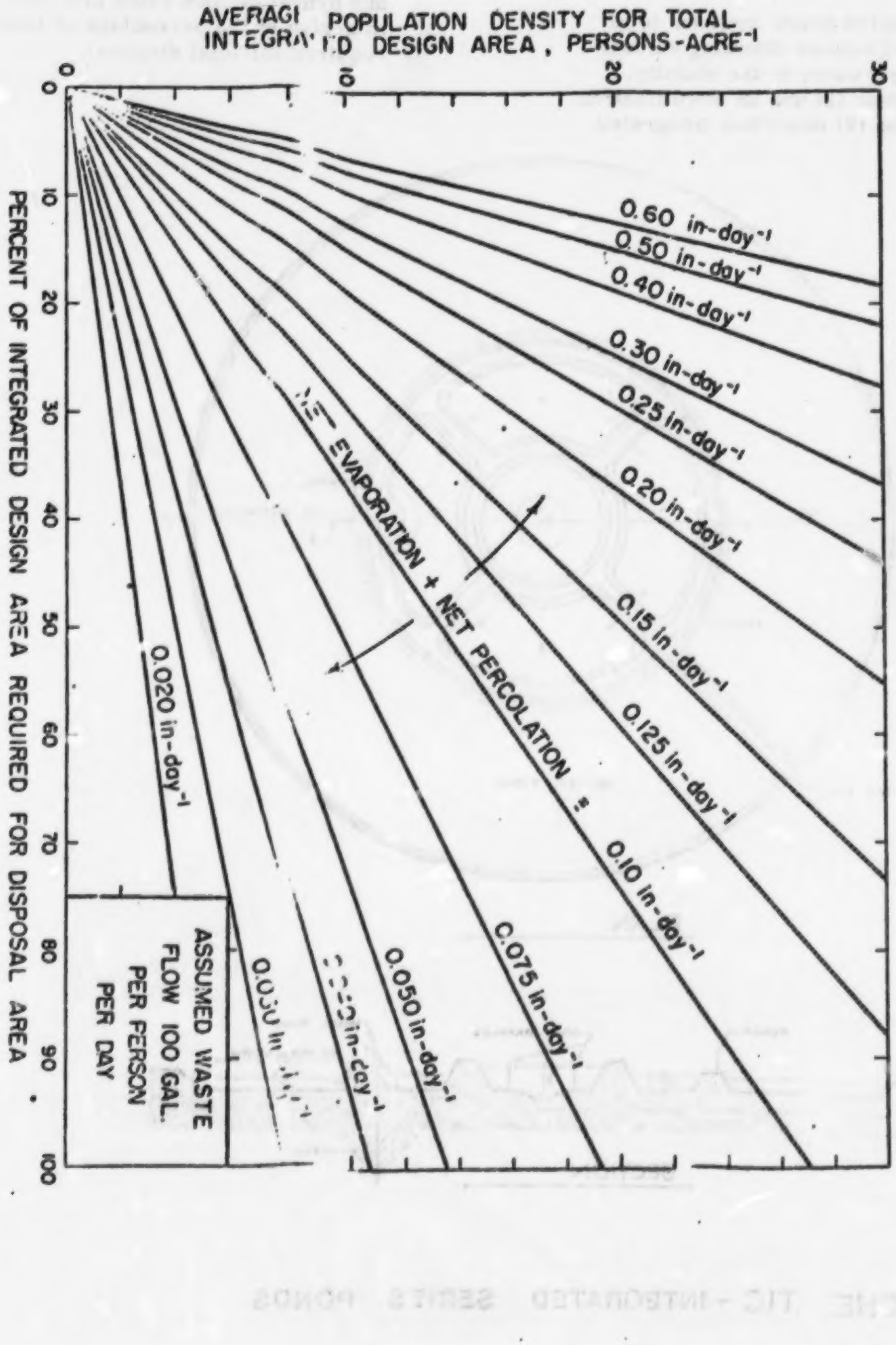
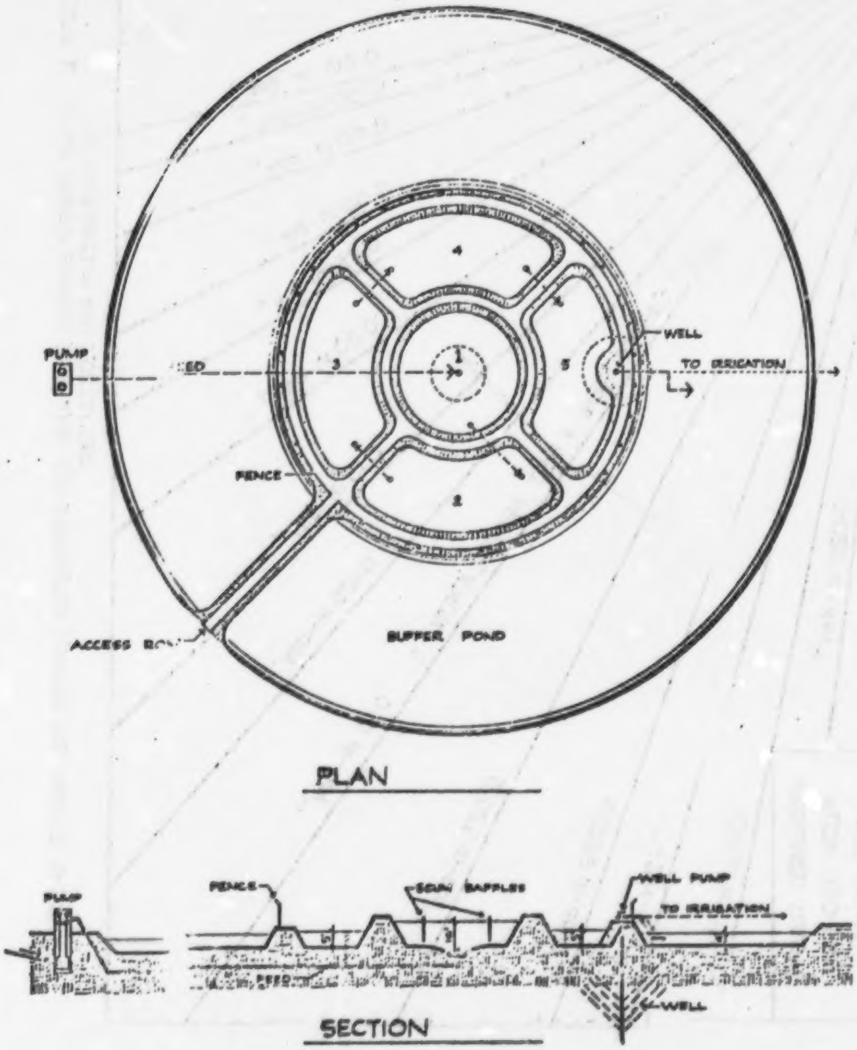


FIGURE 3. RELATIONSHIP BETWEEN POND AREA AND POPULATION DENSITY FOR VARIOUS RATES OF EVAPORATION AND PERCOLATION

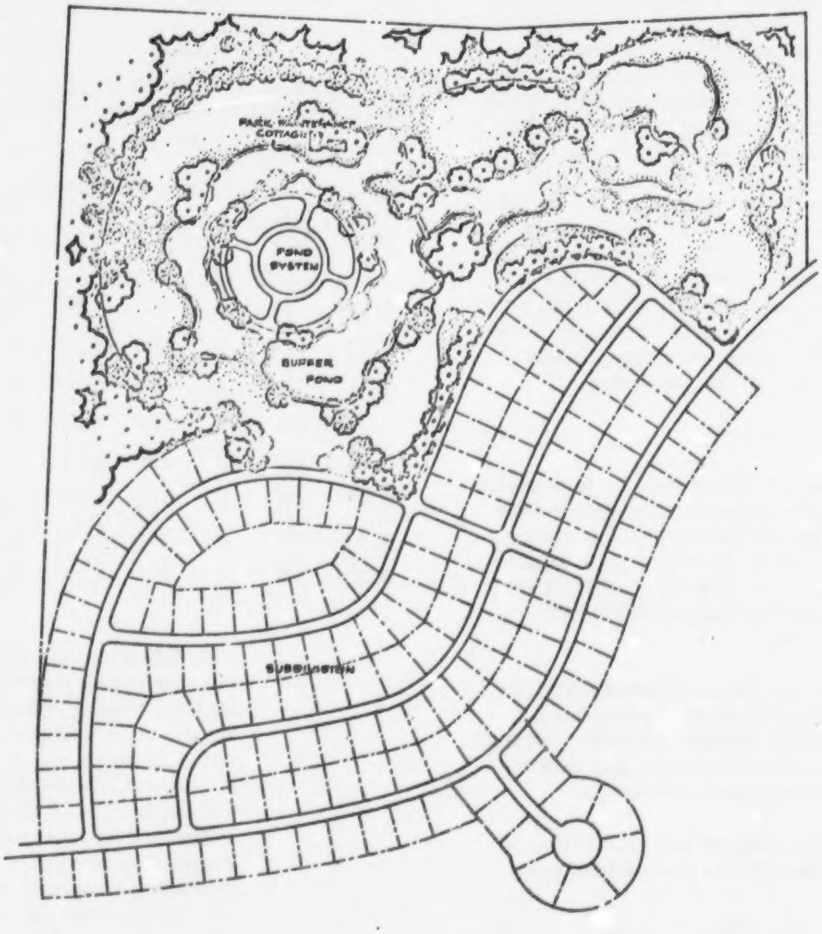
C Pond - Park integrated systems for total disposal.

1 No overflow ponds includes total disposal without affecting surface receiving water in the vicinity. The author (2) and an amplification by Noren (3) describes integrated systems based upon the data in Figure 3 where population density and hydraulic loss rates are used to arrive at the percentage of land required for total disposal.


PUMP
ED
1
2
3
4
5
WELL
TO IRRIGATION
FENCE
ACCESS RO
BUFFER POND
PLAN
PUMP
FENCE
SCUM BAFFLES
WELL PUMP
TO IRRIGATION
FEED
WELL
SECTION

SCHEMATIC - INTEGRATED SERIES PONDS

2 **A typical pond system is outlined in Figure 4 and the position within a subdivision as indicated in Figure 5.**


PARK MAINTENANCE COTTAGE
POND SYSTEM
BUFFER POND
SUBDIVISION

POND SYSTEM IN PARK OF SUBDIVISION DESIGN

3 As pointed out by Noren (3), the park-pond integrated system has several advantages associated with advanced planning. Community sewers are installed in advance in smaller lots than if septic tanks were required. Unit savings in costs of sewers, streets and utilities are significant. Land saved in individual lots may be consolidated into open space held as common use property. Operation and maintenence of the common land uses similar equipment and manpower as park property.

4 The pond complex must be designed for the specific climate soil and population. The integrated pond is more costly than simple ponds. The system is less costly than mechanical plants, however. They require little operational skill but must not be neglected.

D Overflowing Ponds

1 Terminal ponds may be impossible or excessively costly where rainfall greatly exceeds evaporation, percolation is limited, or land is already developed. Intermittent or overflowing ponds may be required.

2 Mass diagrams of predicted flow, evaporation and percolation for seasonal changes must be included to reveal the crucial periods for detention time estimates.

a The critical detention time in days (θ) may be estimated:

$$\theta = \frac{Ad}{Q\ in - A(P_n + E_n)} \qquad (4)$$

where A- is expressed in Acres
d-is depth in ft
Q_{in}- in Acre ft per day
$A(P_n + E_n)$-represents the volume loss function of net percolation and evaporation expressed in ft/day.

b Formula 4 shows that detention increases more rapidly than area and very rapidly as the loss fraction approaches Q in.

c Table III includes relationships of design flow, pond, area, depth, and volume, plotted graphically in Fig. 6.

TABLE III
VARIATION OF DETENTION PERIOD WITH INCREASING POND AREA FOR OVERFLOWING PONDS

Design Flow MGD	Assumed Pond Characteristics Area Acres	Depth ft	Vol Ac-ft	Assumed Q_{in} Ac-ft Day^{-1}	P+E Ac-ft Day^{-1}	Q_{out} O'Flow Ac-ft Day^{-1}	θ Det Per
0.77	5	6	30	2.36	0.3	2.06	14.9
0.77	10	6	60	2.36	0.6	1.76	34.1
0.77	15	6	90	2.36	0.9	1.46	61.5
0.77	20	6	120	2.36	1.2	1.16	103.0
0.77	25	6	150	2.36	1.5	0.86	174.0
0.77	30	6	180	2.36	1.8	0.58	310.0
0.77	35	6	210	2.36	2.1	0.26	810.0
0.77	40	6	240	2.36	2.4	0.00	

d The detention is a function of the integrated factors listed and the events taking place. Evaporation and percolation rates differ in ponds that do or do not contain significant algae but experimental data are insufficient to generalize with respect to detention time. Detention time estimates are only as good as the estimates for P_n, E_n, and flow.

E Treatment of Wastes

1 Significant removal of settleable solids, nutrients, oxygen demanding materials, toxicity, hardness, and pathogens occurs in ponds whether this action is intended or not. Each

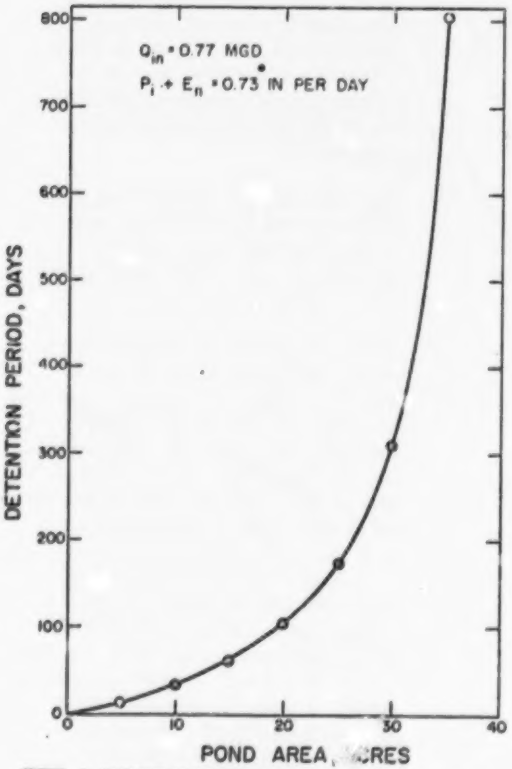


FIGURE 6: VARIATION OF DETENTION PERIOD WITH INCREASING POND AREA FOR OVERFLOWING PONDS

action responds at certain rates that vary with the conditions and reactants. Temperature is a major variable in turn controlled by solar radiation.

a It may be expected that 90% of the settleable material will be removed in 3 days, 99% in 10 days. Growth of algae tends to obliterate the settling record with newly formed suspended solids.

b BOD removal (Table IV) is strongly influenced by temperature in a direct manner. Even at 5°C 90% BOD removal is likely at 100 days. The BOD data may or may not reflect algal activity and newly formed particulates in short time tests.

c Coliform removal is a function of time and temperature in a pond as plotted in Figure 7. Design criteria on coliform removal at low water temperatures may represent + 200 days detention. Coliform group removal is primarily related to pH(7) and generally is the limiting value compared with removal of other indexes.

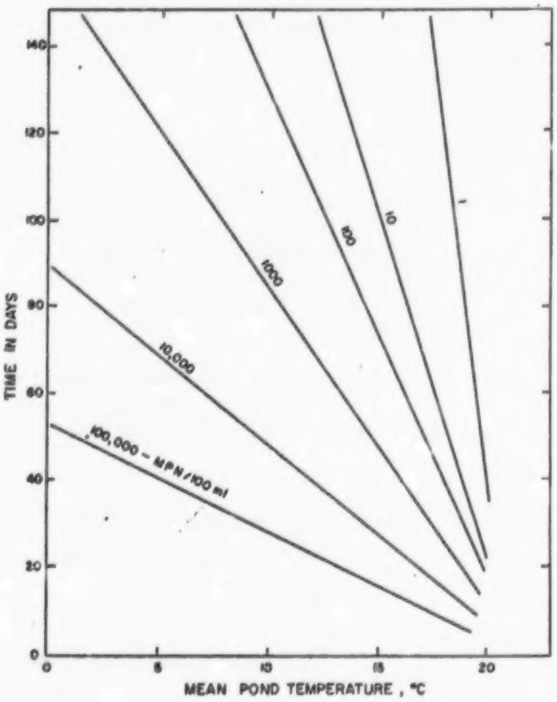


FIGURE 7 OBSERVED MPN/100 ML IN A SINGLE FACULTATIVE POND AS A FUNCTION OF TIME AND TEMPERATURE INITIAL MPN 10^6/ML

TABLE IV

Natural Reduction in Supernatant BOD in an Undisturbed Pond

Time Days	Percent BOD Removal at Indicated Ave. Temp.			
	$10^\circ C$	$14^\circ C$	$15^\circ C$	$18^\circ C$
0	0	0	0	0
1	23	35	47	33
2	40	61	56	53
4	46	70	67	56
9	57	75	75	81
16	72	89	90	87
32	90	90	95	96
64	94	--	94	--

2 Insolubles formed in a pond as a result of biological oxidation and photosynthesis are mutually interrelated in line with oxygen (algal) and CO_2 (bacterial) production.

a Algae production may be approximated (without serious nutrient deficiences by the following:

$$W_a = 0.15\ F\ S\ T_c \qquad (5)$$

where W_A = lbs of algae/A/day

F = photosynthetic efficiency

S = solar energy/day

T_c = temperature coefficient

b The amount of oxygen produced is about 1.5 times the weight of algae and oxygen needed is about 1.6 times BOD requirements. Oxygen production also can be estimated from Eq5.

c Table V presents solar energy tabulation by month and latitude. Whenever solar energy is below 100 cal/sq cm/day, low or freezing water temperatures are likely and photosynthesis is negligible.

d Non overflow ponds are stressed because algal production releases oxygen during rapid growth. O_2 demand of algal cell mass decay comes later.

e Table VI presents relationships of K_T with temperature for a specific organism strain. General behavior is fairly well established, but specifics are not. This table shows maximum activity but it is not certain that this holds for all situations and organisms.

f Photosynthetic efficiency is highly variable and important in prediction of oxygen production. Mean efficiency in outdoor ponds at $20^\circ C$ tends to be about 4%. The efficiency of completely mixed cultures declines with increasing light intensity and duration and increases with depth up to a depth of about 3 times the depth of light penetration. Net photosynthesis within a given algae cell is a resultant of two variable functions of photosynthesis and respiration, i.e.,

$$P\ net = (P - R) \qquad (6)$$

TABLE V

PROBABLE VALUES OF VISIBLE SOLAR ENERGY AS A FUNCTION OF LATITUDE AND MONTH

Latitude	Month											
	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
0 max	255[a]	266	271	266	249	236	238	252	269	265	256	253
min	210	219	206	188	182	103	137	167	207	203	202	195
10 mas	223	244	264	271	270	262	265	266	266	248	228	225
min	179	184	193	183	192	129	158	176	196	181	176	162
20 max	182	213	246	271	284	284	282	272	252	224	190	182
min	134	140	168	170	194	148	172	177	176	150	138	120
30 max	136	176	218	261	290	296	289	271	231	192	148	126
min	76	96	134	151	184	163	178	166	147	113	90	70
40 max	80	130	181	181	286	298	288	258	203	152	95	66
min	30	53	95	125	162	173	172	147	112	72	42	24
50 max	28	70	141	210	271	297	280	236	166	100	40	26
min	10	19	58	97	144	176	155	125	73	40	15	7
60 max	7	32	107	176	249	294	268	205	126	43	10	5
min	2	4	33	79	132	174	144	100	38	26	3	1

[a] Values of S in cal per sq cm per day.

To determine average value of S: $S_{ave} = S_{min} + p(S_{max} - S_{min})$ in which

p = total hr sunshine divided by total possible hrs sunshine.

To determine yield of algal cell material in lb of algal cell material per acre per day:
Y = 0.15 FS. This formula applies to a mean temp. of 20°C.
For other temperatures apply temperature coefficients from Table 5.

To determine yield of oxygen in lb of oxygen per acre per day: $O_2 = 0.25$ FS.

This formula applies to a mean temperature of 20°C. For other temperatures, apply temperature coefficients from Table 5.

TABLE VI

TEMPERATURE COEFFICIENTS FOR CHLORELLA PYRENOIDOSA* GROWN IN SEWAGE

Temp°C	k_T	Temp°C	k_T
0	0.00	18	0.96
2	0.00	20	1.00
4	0.00	22	0.99
6	0.02	24	0.96
8	0.23	26	0.92
10	0.49	2	0.87
12	0.70	30	0.80
14	0.82	32	0.73
16	0.91	34	0.65

*Emersion strain

The cells are the products of (P - R). Few have studied respiration rates of photosynthesizing algae. McCarthy & Forwe (14) found that cells in a dark aerobic environment lost about 3% of dry wt/day. The author observed rates 10 to 20 times that at 25 to 30°C.

3 Nutrient removal

a The conversion of soluble nutrients to removable particulate form is an obvious means of nutrient removal. Off gas CO_2 removal is significant if algal fixation is limited. Methane fermentation, nitrogen oxidation and denitrification, phosphorus and calcium carbonate precipitation are significant. Other mechanisms are possible.

b Detailed discussion of methane fermentation is not intended herein (see 4, 5). The general formula for fermentation gas production in ponds is

$$G = 450\,(T - 15) \qquad (7)$$

where G = gas emission cu.ft./A./day
T = temperature in °C

Gas production occurs below 15°C but temperature dependence is irregular. Emitted gas composition indicates takeout of about 1 lb BOD/10 cu.ft. of evolved gas. Gas emission results in carbon takeout in the form of methane or carbon dioxide.

c Deep facultative ponds are receiving renewed interest because of the takeout of up to 80% of the combined nitrogen content in process. This is the cheapest available method for nitrogen removal. Solids removal accounts for part of this. Nitrification of unoxidized nitrogen in aerobic zones of the pond followed by denitrification in deeper waters of the pond may result in release of molecular nitrogen. The nitrate oxygen is used for respiratory demand in DO deficient water. Other mechanisms may be included but the two mentioned are significant.

d Phosphorous removal by precipitation as a hydroxy phosphate occurs in high pH waters. Mineral content of the incoming water influences phosphate conversion and form. Biological factors including luxury uptake of P on cell mass are important. It is not possible to generalize precise behavior of P in a complex and changing situation. Recycle characteristics of P complicate interpretation and prediction.

e Sobsey (8) observed that the presence of algae favored an increased removal of viruses in stabilization ponds.

f Klein and Kaufman (9) reported almost complete destruction of NTA.

g Reclamation aspects of ponds with respect to nutrient water and land are well documented by Dryden and Stern (10), Oswald (11 & 12) and McGarry (13).

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This outline was prepared by William J. Oswald, Ph. D., Professor of Sanitary Engineering and Public Health, University of California, Berkeley, CA.

SMALL TREATMENT SYSTEMS
(PACKAGE PLANTS)

I DEFINITION

A Preassembled Units from Factory

B Sizes from 150,000 gpd to Individual Homes

II TYPES (Figure 1)

A Complete-Mix Extended Aeration

B Contact Stabilization

C Trickling Filters

III MANUFACTURERS

A More than 20 Different Firms make Package Treatment Plant Units

B Extended Aeration Most Common

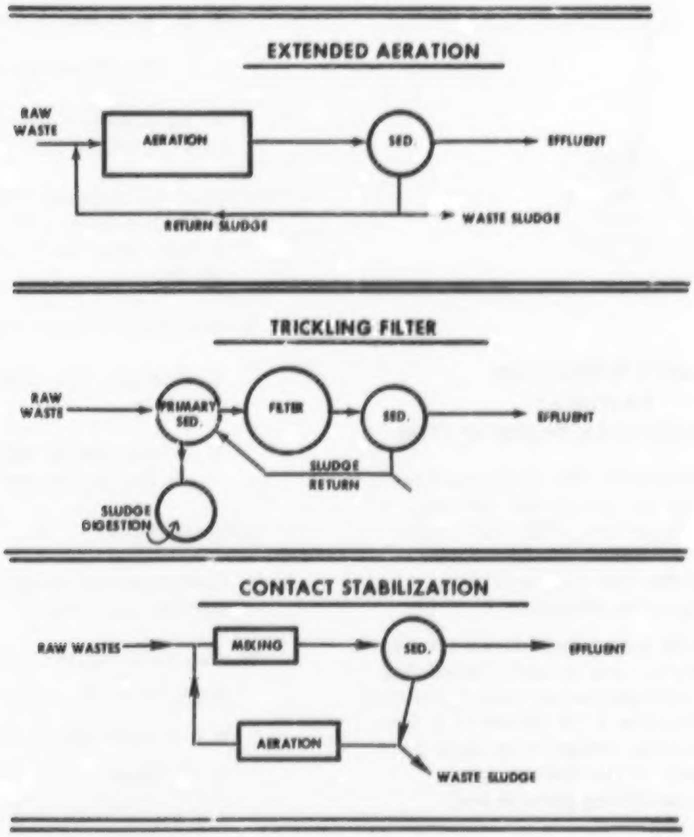
IV EXTENDED AERATION PLANTS

A Use

1 Survey in 1960 indicated 1224 plants in the states.

2 Most served schools, motels, industries, etc.

Figure 1


EXTENDED AERATION

TRICKLING FILTER

CONTACT STABILIZATION

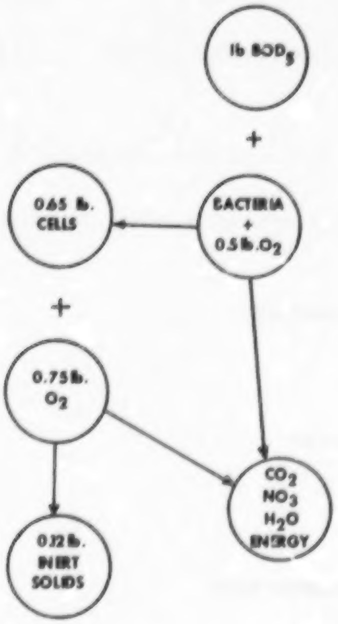
RAW WASTE
AERATION
SED.
EFFLUENT
RETURN SLUDGE
WASTE SLUDGE
RAW WASTE
PRIMARY SED.
FILTER
SED.
EFFLUENT
SLUDGE RETURN
SLUDGE DIGESTION
RAW WASTES
MIXING
SED.
EFFLUENT
AERATION
WASTE SLUDGE

B Process Theory

1 Soluble BOD removal

a Organic matter is used by bacteria in new cell synthesis and basic metabolism. Figure 2 illustrates path of one pound of domestic sewage in a total oxidation system.

Figure 2



BOD REDUCTION PATHWAY COMPLETE OXIDATION SYSTEM

b Figure 3 illustrates the BOD removal curve and the rate of solids buildup with time and F/M ratios. The F/M ratio is the food to microorganism ratio or lb BOD_5/ lb MLVSS (mixed liquor volatile suspended solids).

NOTE: Solids go through three phases in their growth - log growth, declining growth and endogenous or auto oxidation. McKinney reports F/M ratios of 2.5 to 0.006 as defining range of declining growth phase. Extended aeration operates in declining growth and endogenous phases.

2 Solids accumulation

a Solids accumulate until system is in equilibrium or separate sludge wasting is employed. Otherwise, solids wasted from system as they are formed.

b Expressed by relation

$A = (aL_r - bMd) + Si - S$

A = accumulation of solids

a = fraction of food synthesized (approx. 0.65 for domestic sewage)

L_r = lb BOD_5 removed/day

b = fraction of solids oxidized/day

Md = mass of degradable solids in system

Si = inert solids entering system

S = lbs of solids wasted/day

c At equilibrium oxidation of 1 lb of BOD_5 results in 0.12 lb of inert solids

d Study at National Science Foundation indicated it took 36 to 49 days to build solids to desired level of 2500 mg/l. MLSS.

e Methods to lower startup time include

1) Seeding with sludge from another plant

2) Allow unit to operate as a primary plant for 1 week

3 Effluent BOD

a Composed of soluble portion and portion in solids

b Can be computed from relation

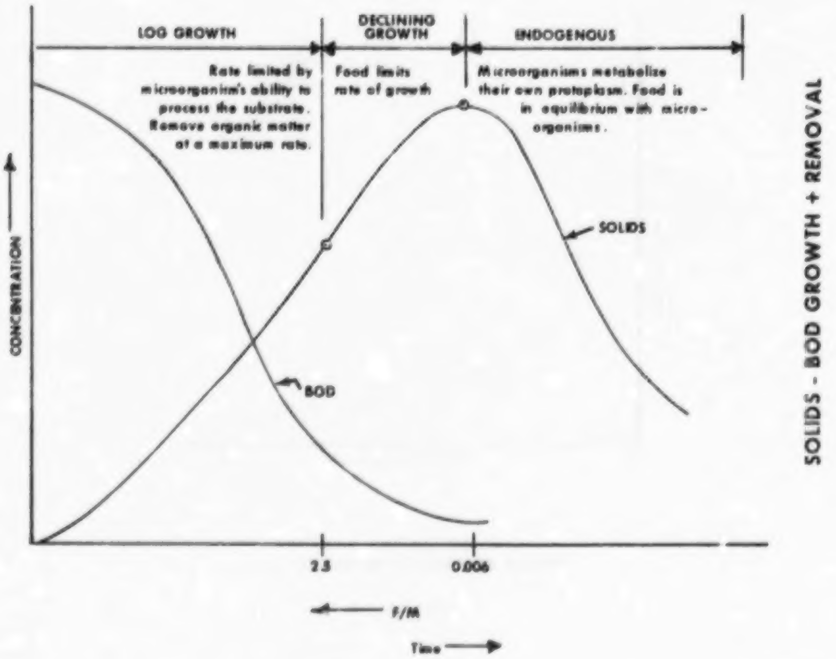
Effluent BOD_5 = L + CS

S = effluent susp. solids

L = effluent soluble BOD_5

C = mg/l BOD_5/mg/lSS (suspended solids)

Figure 3



c Soluble BOD_5 in effluent is function of:

1) Detention time
2) Temperature
3) MLVSS(Sa)
4) lbs of BOD_5 removed/lb MLVSS-day

d Soluble BOD_5 can be computed from the relation

$$L/Lo = 1/1 + KS_a t$$

L = effluent soluble BOD_5

L_o = influent soluble BOD_5

K = lb BOD_5 removed/lb MLVSS-day

S_a = MLVSS

t = Detention time, days

K is a function of temperature and effluent BOD_5. It can be estimated from the relation

$$K = \frac{C_1 L}{C_2 + L} \text{ day}^{-1}$$

where $C_1 = 0.1$ and $C_2 = 80$ for domestic sewage.

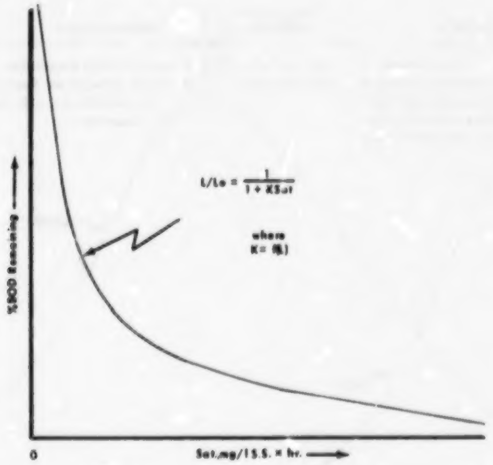
Temperature effect can be measured by

$K_t = K_{20} - O^{T-20}$ where O is approximately 1.0 - 1.04 for activated sludge systems.

Figure 4 illustrates a typical BOD removal

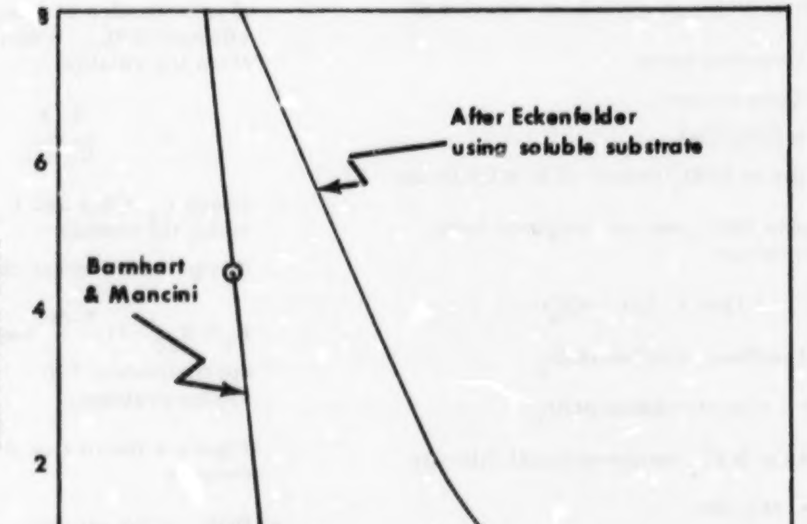
e BOD_5 of the effluent solids will vary with aeration time or sludge age. Wide variation is reported as illustrated on Figure 5.

Figure 4



TYPICAL BOD REMOVAL CURVE

Figure 5



4 Nitrification

a Follows the equation

$$NH_3 + 2O_2 \longrightarrow NO_3 + H_2O + H^+$$

b Significant for following reasons:

1) Stream pollution due to oxygen demand. Approx. 1 lb NH_3 will require 1.9 lb O_2 in the complete oxidation cycle. Complete nitrification may be required by the states.

2) pH problems in aerator if waste is not highly buffered; i.e. 1 lb of NH_3 that is nitrified will require 5.9 lb of alkalinity as $CaCO_3$.

3) Chlorine demand of NH_3 is approximately 8.35 lb Cl_2 per lb of NH_3 in effluent. If chlorination is practiced and a free residual required, it is very important to obtain complete nitrification.

c A highly nitrified effluent will cause floating sludge problems in the final clarifier if the sludge goes anaerobic. This is due to evolution of nitrogen gas according to relation

$$2NO_3 \longrightarrow 3O_2 + N_2 \uparrow$$

5 Solids separation

a Controlling factor in overall performance of system. If solids washed out in the effluent, BOD is high.

b Settling characteristics of sludge is a function of:

1) Aeration solids concentration

For activated sludge settling rates will vary from 20 - 30 ft/hr at 1000 mg/l MLSS to 5 - 6 ft/hr at 4000 mg/l MLSS.

2) Organic loading

At F/M ratios above 2 and less than 0.2, have dispersed organisms and poor settling.

At F/M ratios 0.35 to 1.0 filamentous organisms develop and poor settling results.

6 Temperature

a Effects the metabolism rate of all microorganisms

b Can be estimated from Arrhenius equation

$$K_t = K_{20}\ \text{-O}^{\,T-20}$$

or

$$b_t = b_{20}\ \text{-O}^{\,T-20}$$

K_t or b_t = reaction rate at Temp. T

K_{20} or b_{20} = reaction rate at 20° C

c Values of -O vary with type of system

d Values of -O reported are

Process	-O	Source
Activated sludge	1.0 - 1.04	Wuhrman
Trickling filters	1.035	Howland
Aerobic lagoons	1.035	Sawyer
Aerobic-facultative lagoons	1.07 - 1.08	Mancini & Barnhart

C Pros and Cons

1 Pros

a Small land area

b No dependence on adsorption underground

c Small hydraulic head loss

d Adaptable to variety of topographical and climatic conditions

e Prefab units available in many sizes

f Fast and relatively low-cost field installations

g Located near facility served

h No sludge digestion problems

i High degree of treatment with proper operation

j No odors generally

2 Cons

a Requires constant operation and maintenance

b Power costs high

c Cost of treatment high

D Design

1 State requirements will generally dictate design. Typical values are listed below.

a Aeration tank

1) Detention time - 24 hr

2) Organic loading - 15 - 25 16 BOD_5/1000 ft^3

3) Air - 1,500 - 2100 ft^3/16 BOD removed

b Settling tank

1) Detention time - 4 hr

2) Surface overflow - 200-600 gpd/ft^2

3) Weir discharge - 600 - 2,600 gpd/ft

4) Sludge return pumping capacity 3 × average daily flow

E Efficiencies

1 Laboratory data from 59 of 1224 plants surveyed by PHS show a wide range of efficiencies

BOD_5 - 99.3 to 33.3 average 86

SS - 96.5 to 0 average 62

2 Related directly to operation and more specifically solids

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This outline was prepared by B. David Clark, Sanitary Engineer, Pacific Northwest Water Laboratory.

ADVANCED WASTE TREATMENT PLANTS FOR TREATMENT OF SMALL WASTE FLOWS

INTRODUCTION

During the last two decades, the need for waste treatment in localities where connection to a centralized system is not possible or economically feasible has become more and more urgent. Typical examples include suburban housing developments, institutions, rest areas along highways, tourist areas in parks, isolated work camps, etc. In these situations the flow is low because the population served is limited, and consequently such plants are referred to as "small flow" treatment plants. As a rule of thumb, plants in excess of 500,000 gal/day capacity (equivalent population 5,000) are considered outside the "small flow" class. This size limit is based on limitations of shop fabrication and typical sizes of communities not connected to regional sewerage systems, but is somewhat arbitrary. Data on the number of plants of this type which will be required in the near future are virtually non-existent. Table 1 presents some estimates of the present "market" for such plants. An overall estimate of the significance of this problem is given by the data of Smith which show that 10% of the total weight of BOD in municipal sewage discharges is generated in communities with a population below 5,000.

TABLE 1
Estimates - Small Flow Treatment Plant Needs

Category	Estimated No. of Plants
Small Communities	3,000 - 6,000 [(a)]
Parks and Marinas	2,000 - 10,000[(b)]
Alaskan Work Camps & Eskimo Villages	500 - 2,000

(a) The Economics of Clean Water - Vol. I, USDI, March 1970

(b) Personal Communication - U.S. Park Service

PERFORMANCE CRITERIA

The "small flow" treatment plant market has not been ignored by commercial interests. During the last 20 years they have installed approximately 5,000 package sewage treatment plants. These have all been designed on the basis of biological treatment technology and for the most part they have done the job required. However, these plants are limited in applicability. In many locations, which shall or already do require "small flow" systems, one or more of the following conditions can be expected which will exclude the use of a purely biological unit:

a Toxic materials in the waste

b Extreme diurnal flow and load variation

c Requirement for nutrient removal

d Requirement for start and stop operation

e Reuse of the treated effluent

A pertinent example of the inability of biological package plants to meet recent upgrading in treatment criteria is given by the recent action of several localities halting subdivision home construction pending the installation of adequate waste treatment. Biological package plants did not meet the stringent effluent criteria established by these local governments.

Waste treatment technology which can meet the stringent performance criteria for small flow plants has been under development in the Advanced Waste Treatment program for the last decade. These new methods are primarily physical and chemical in nature rather than biological. Demonstration of these concepts on a large scale (> 10 mgd) is soon to take place. As these systems have worked well in pilot plants, it is reasonable to assume they shall do so in "small flow" systems. These pilot plant studies were conducted on typical domestic sewage. Although small flow wastes are in general stronger than typical domestic sewage they are not fundamentally different in character. Table 2 compares the characteristics of typical small flow wastes and typical domestic sewage.

SMALL FLOW ADVANCED WASTE TREATMENT PLANTS

A Basic Design Consideration

Treatment of small flow wastes may require one or more of the following steps: suspended solids removal, dissolved organic carbon removal, nitrogen and/or phosphorus removal, and disinfection.

The Advanced Waste Treatment program has developed one or more processes to meet each of these treatment requirements. However, design of a treatment train cannot be predicated only on achieving a desired effluent quality but must be concerned with reliability and cost. On these latter points conditions are somewhat different when comparing small volume and conventional flow plants. Because of the highly variable nature of the wastes to be treated a premium must be placed on processes which function well regardless of waste variability. A second factor to consider is the apportionment of total cost between capital and operation. In most "small flow" situations a full-time operator is not economically feasible, thus a treatment system with a relatively high capital expenditure for automation can be justified.

Based on the special requirements of small flow treatment plants discussed above, three generalized treatment trains have been selected as worthy of consideration for future development.

TABLE 2

TYPICAL "SMALL FLOW" WASTE CHARACTERISTICS

	Typical[a] Municipal Sewage	Household[b] Wastewater	Household[c] Wastewater	Winter[d] Recreation Area
Suspended Solids, mg/l	200	376	173	342
COD, mg/l	350	776	450	790
BOD, mg/l	210	435	222	390
Total Nitrogen, mg/l--N	33	84	67	78
Ammonia Nitrogen, mg/l--N	12	64	--	23
Total Phosphate, mg/l PO_4	24	61	49	32
Grease, mg/l	14	68	92	--

(a) Water Supply & Sewerage, Steel, E.W., McGraw Hill - 1960

(b) Watson, et al., JWPCF, 39, 2039 (Dec. 1967)

(c) Clark, B.D., "Houseboat Waste Characteristic & Treatment," PR-6, FWQA (Sept. 1967)

(d) Clark, B.D., "Basic Waste Characteristics at Water Recreational Areas, PR-7, FWQA (Aug. 1968)

B Physical-Chemical System

Figure 1 illustrates a wholly physical-chemical treatment system employing chemical clarification followed by carbon adsorption. Either powdered or granular activated carbon can be utilized. The system performance is quite flexible in that the degree of treatment obtained can be varied by the use of optional filtration steps and by altering dosage of chemicals or powdered carbon or the frequency of replenishment of granular carbon. In some cases activated carbon treatment may not be required as chemical clarification consequently yields 70% to 75% COD removal from raw sewage. It is anticipated that only for the largest of these plants the cost of discarding carbon after one use appears less than the required capital expenditure for a regeneration system.

Chemical clarification with a sufficient dose of iron or aluminum salts or lime can provide any degree of phosphorus removal required. In general, the extra chemical cost associated with dosages to the level required for phosphorus removal is relatively minor in the overall cost figures for small volume treatment systems. In addition, dosage to this level will always assure excellent clarification.

Ammonia nitrogen removal is not provided for specifically in this scheme. The most feasible method for nitrogen removal would be breakpoint chlorination, because it is the method which requires least attention from an operator. Thus effluent disinfection and ammonia nitrogen removal can be achieved in one step. However, a significant increase in chloride ion can be expected in the effluent.

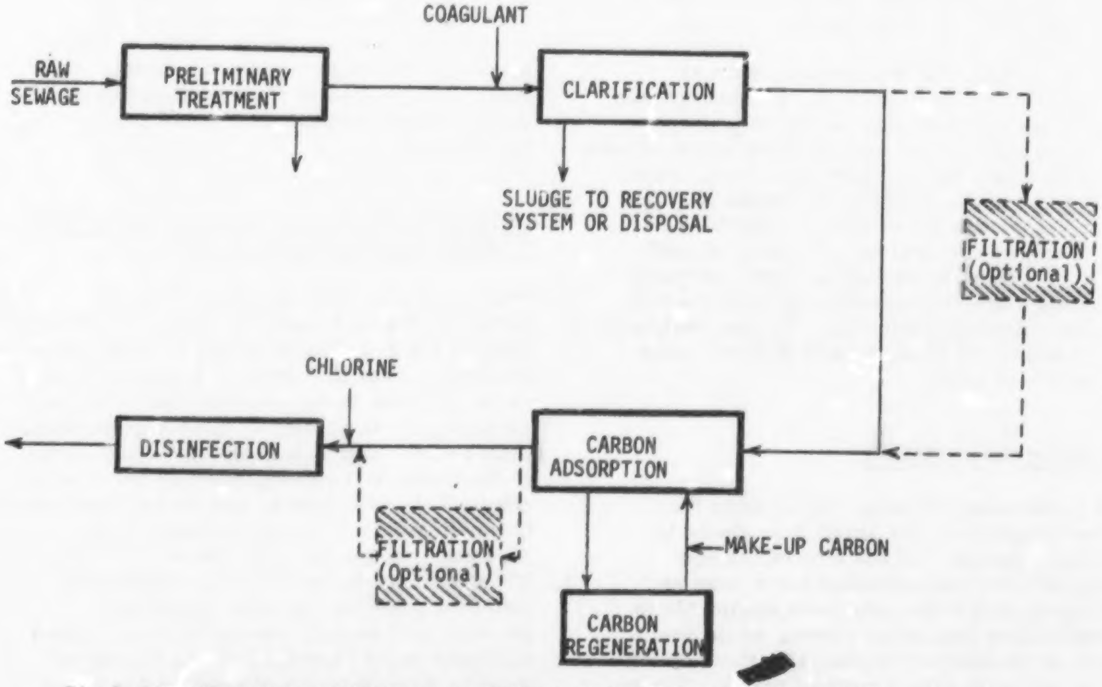
COAGULANT
RAW SEWAGE
PRELIMINARY TREATMENT
CLARIFICATION
SLUDGE TO RECOVERY SYSTEM OR DISPOSAL
FILTRATION (Optional)
CHLORINE
DISINFECTION
CARBON ADSORPTION
FILTRATION (Optional)
MAKE-UP CARBON
CARBON REGENERATION

Fig.1. SCHEMATIC FLOW DIAGRAM OF A PHYSICAL-CHEMICAL TREATMENT SYSTEM

C Ultrafiltration System

The second general treatment scheme is illustrated in Figure 2. This provides for a variety of optional pretreatment steps leading to an ultrafiltration membrane assembly. A membrane providing total suspended solids capture with some degree of dissolved organic removal would be utilized. In essence, the role of the membrane in these systems is to function as a polishing or safety device which will produce a consistent effluent quality regardless of fluctuations in the raw waste. The pretreatment steps serve to reduce the load on the membrane and reduce the rate of membrane fouling.

D Chemical-Biological System

Figure 3 illustrates a chemical-biological treatment system. This treatment train is less generally applicable than the others in that it is heavily oriented to biological treatment. It is only applicable where neither toxicity nor flow interruption is anticipated. In this system mineral addition to the aerator is included not only for phosphorus removal but to prevent biological solids loss from the sedimentation tank under varying hydraulic load. Provision of an automatic backwash deep bed filter serves as an effluent polishing device. Nitrogen removal may be obtained with this system by operation of the activated sludge system such that nitrification will take place and injecting sufficient methanol ahead of the filter so that denitrification will take place.

SLUDGE TREATMENT

As is the case for large scale plants the greatest problem for small flow plants is sludge disposal. Of the several sludge disposal methods available some such as sludge drying beds, are more applicable to small plants than large plants, while some such as mechanical sludge filtration appear to be too expensive for small plants. Treatment and disposal methods which are being seriously considered include:

a Dewatering on drying beds with or without lime treatment

b Gravity thickening and temporary storage with periodic pump-out

c Incineration

d Aerobic digestion

Incineration is the most costly of these but the most attractive as the only residue for disposal is a sterile ash. A fluidized bed incineration system which has been successfully applied to the incineration of plastic wastes will soon be evaluated for incineration of sludge. This system shows promise for small treatment plants because fluidized beds hold their temperature well during shutdown on several days, and are relatively easy to automate.

Our knowledge of fundamental characteristics of the chemical-biological or chemical raw sewage solids sludges which will result from small flow systems is not as extensive as our knowledge of conventional primary and secondary sludges. These data will be required in order to design sludge handling systems. In future research activities in the small flow treatment plant field, gathering data on sludge handling will be of prime importance.

CURRENT MODELS OF SMALL ADVANCED WASTE TREATMENT PLANTS

There are very few examples of small Advanced Waste Treatment plants which are commercially available at the present time. However, these are worth discussing in some detail in order to demonstrate their inherent advantages. In principle, physical-chemical plants differ basically from biological plants in that they can be designed to be much more compact than the latter, and so lend themselves better to small or modular installations. Moreover, since all such Advanced Waste Treatment plants consist of 2-3 distinctly different physical-chemical treatment processes in series, obviously these varied elements can be assembled in a variety of ways to serve any specific desired purpose and to minimize space requirements. An array of processes is available to effect: solids removal, organic removal, nutrient removal, and, where necessary, some degree of inorganic removal.

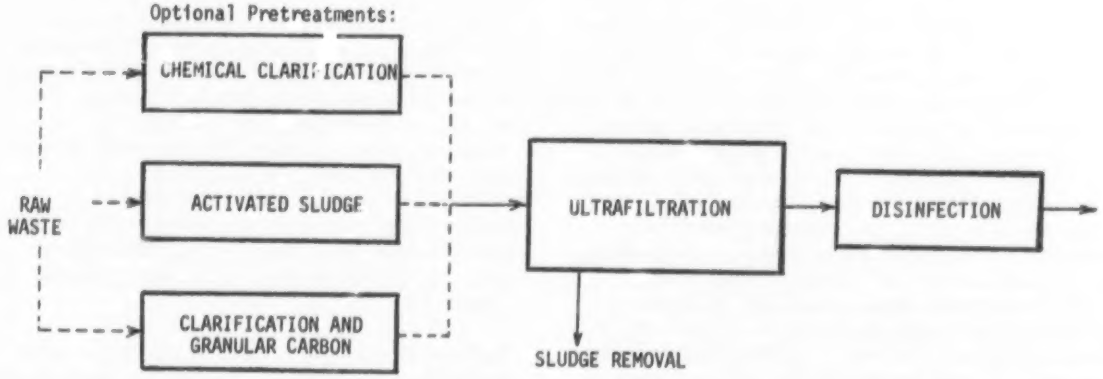
Optional Pretreatments:
CHEMICAL CLARIFICATION
ACTIVATED SLUDGE
CLARIFICATION AND GRANULAR CARBON
RAW WASTE
ULTRAFILTRATION
DISINFECTION
SLUDGE REMOVAL

FIGURE 2. SCHEMATIC DIAGRAM OF ULTRAFILTRATION SYSTEM

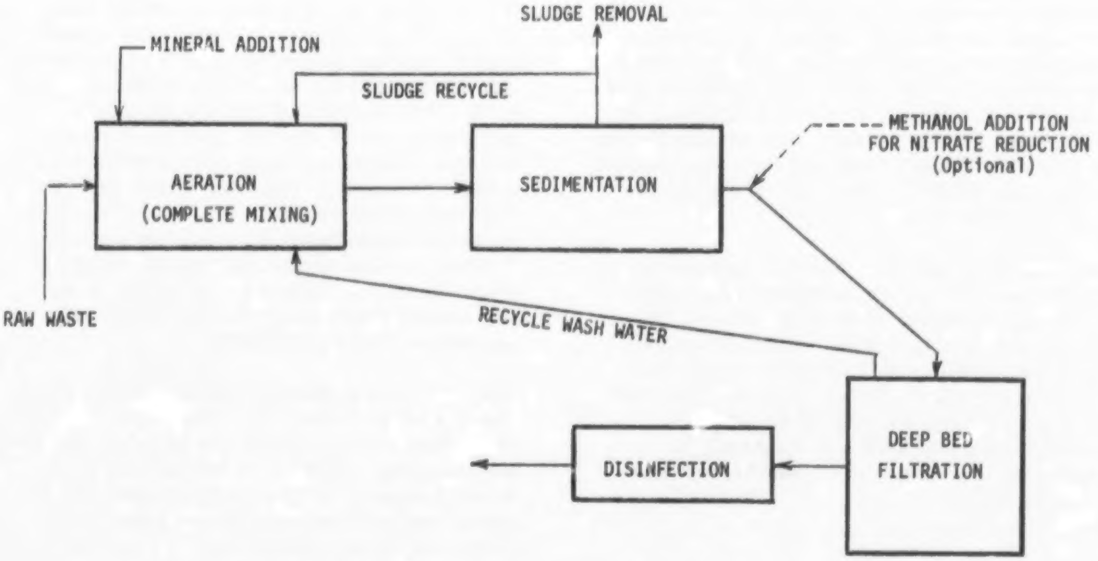
SLUDGE REMOVAL
MINERAL ADDITION
SLUDGE RECYCLE
METHANOL ADDITION FOR NITRATE REDUCTION (Optional)
AERATION (COMPLETE MIXING)
SEDIMENTATION
RAW WASTE
RECYCLE WASH WATER
DEEP BED FILTRATION
DISINFECTION

FIGURE 3. SCHEMATIC DIAGRAM OF CHEMICAL-BIOLOGICAL SYSTEM

Since even biological processes require solids removak, it is possible (as we shall see) to substitute an Advanced Waste Treatment process for the traditional gravity settling to effect an improvement in a biological package plant, both in terms of treatment efficiency and space requirements. There are several small plants with which we have some experience. The small Advanced Waste Treatment plants which we shall consider are of interest for three basic reasons: 1) they represent several distinctly different process sequences; 2) they represent some of the combinations of the physical-chemical treatment processes which are most likely to be applied in the future, both at large or small scale; and 3) they demonstrate applications in situations where small Advanced Waste Treatment plants hold great promise for the future. Four different plants shall be considered, three of which have been tested at a commercially applicable scale, and the other of which is still being tested in the laboratory.

CLARIFICATION-CARBON TREATMENT

The most popular physical-chemical treatment design currently being evaluated consists of chemical clarification followed by granular activated carbon adsorption, with or without an intermediate filtration step. (See Figure 1) The Met-Pro Water Treatment Company of Lansdale, Pennsylvania*, has designed a unit of this type (Model 1100-10) for the treatment of laundry wastes. However, the plant has wider applicability.

The Met-Pro unit (see Plate 1) consists of an upflow solids contact clarifier followed by two-stage granular carbon treatment: the first stage is a downflow column of carbon on an anthracite coal base and the second stage is an upflow carbon column. The unit is rated at about 24,000 GPD. In our evaluation of this unit at Cincinnati, a comminuted and degritted wastewater was dosed with any of several coagulants just prior to entry into the sludge blanket, where the retention time was about one hour. Supernatant overflowed a weir onto a 33" deep bed of carbon (12 × 40 mesh) at a rate of between 1.3 and 2.5 gpm/sf. The second (upflow) stage had the same amount of carbon as the first, and the empty bed contact time for both stages was 16-32 minutes for our range of flows. Carbon effluent was used to backwash the upflow carbon bed. The operation is countercurrent in that spent carbon from the upflow bed is used to replace spent carbon from the preceding downflow bed. Spent carbon from the first contactor is discarded.

Before proceeding to the results of the plant evaluation, we should consider the application intended for the plant so that the data can be put in proper perspective. The situation is typical of many for which this and similar small plants are envisioned, i.e., a remote area where no other waste treatment facilities are within reach and where some degree of water reuse is projected because water supply is either in short supply or expensive.

The North Slope of Alaska is a developing area of oil production. Being remote and highly susceptibel to the effects of pollution, a treatment-reuse scheme is a desirable goal. The Met-Pro plant was thought suitable to serve the needs of work camps and two such plants have been installed for waste treatment. The total water use of a 300-man camp might be 30,000 GPD. The principal opportunity for reuse is for toilet-flushing, which would not require drinking water quality. This use represents a very significant fraction of the total water use, perhaps 6,000-8,000 GPD.

The Met-Pro plant was operated during 3-4 months on an 8-hour-per-day basis. This permitted us to evaluate the effect of starting and stopping. About 200,000 gallons were treated as part of 26 separate runs which tested various coagulants, dosages, flow rates, and raw wastewaters. A summary of the results is shown in Table 3.

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*Mention of commercial products does not imply endorsement by the Office of Water Programs, Environmental Protection Agency.

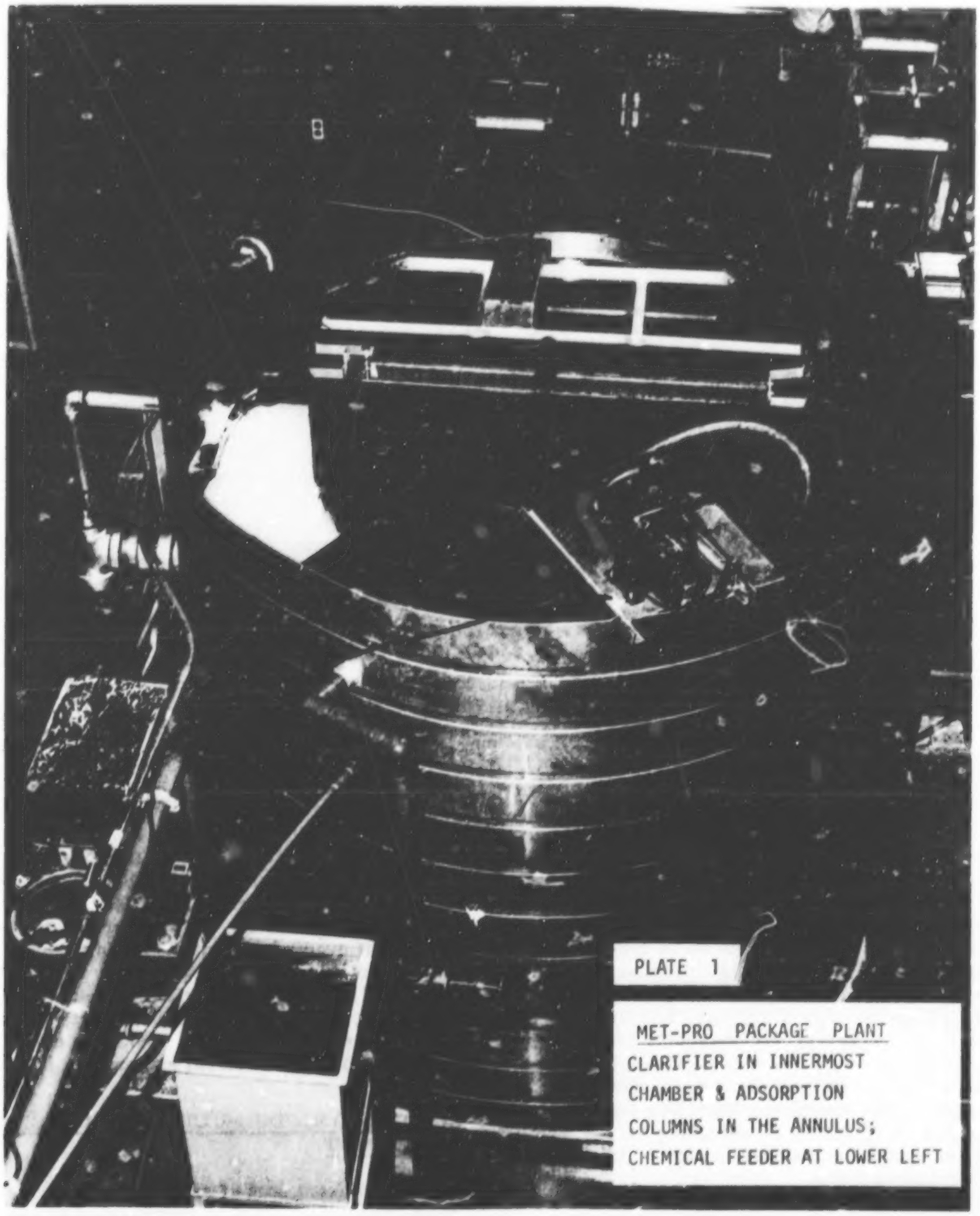

PLATE 1

MET-PRO PACKAGE PLANT
CLARIFIER IN INNERMOST
CHAMBER & ADSORPTION
COLUMNS IN THE ANNULUS;
CHEMICAL FEEDER AT LOWER LEFT

TABLE 3

SUMMARY OF PERFORMANCE OF THE MET-PRO CLARIFICATION-CARBON PACKAGE PLANT

(OWP, CINCINNATI, OHIO)

	Average Values, mg/l		
Parameter	Influent	Effluent	% Removal
COD	330	17	95
Color (Units)	48	8.3	83
Turbidity (JTU)	91	2.5	97
pH	7.6	---	--
TSS	151	---	--
Total P	6.7	<1.1	--
Ammonia -N	21.1	13.3	--
Organic -N	7.8	1.6	--
Total Count (Per ml)	6.45×10^6	170,800	97.4
Total Coliform (Per ml)	278,000	1,418	99.5
Fecal Coliform (Per ml)	59,000	175	99.7
Fecal Streptococci (Per ml)	13,840	91	99.3

Results for all the runs were averaged. The organic effluent level is obviously much superior to biological secondary effluent. Microbiological quality is still somewhat poor and disinfection might be in order. Some idea of the variability of influent and effluent characteristics can be gained from the graphs showing frequency distributions for COD, turbidity, and phosphate (Figures 4-6). It should be noted that both COD and turbidity are always at least of secondary effluent quality. The sharply inclined line for PO_4 effluent is obviously meaningless here because high PO_4 values are due to inadequate coagulant dosages.

The chemical costs are given in Table 4. The costs are FOB and do not include freight.

Poliovirus I inactivation by disinfection was evaluated and the results are given in Table 5. Two separate trials were made using both iodine and chloramine. It is important to notice that even where water is being used for non-potable purposes, the water must be thought of as potentially for human contact. Therefore, aesthetic and microbiological criteria are just as much of a concern as solids and organic removal standards.

ACTIVATED SLUDGE-ULTRAFILTRATION TREATMENT

A quite different sort of small Advanced Waste Treatment plant is represented by the biological "package" plant which has been upgraded by addition of an Advanced Waste Treatment process. The IOPOR System is manufactured by Dorr-Oliver, Inc., of Stamford, Connecticut.* It consists of a high solids activated sludge process followed by an ultrafiltration membrane for complete solids separation. The use of the membrane to replace settling or conventional filtration is intended to conserve space and to achieve a higher solids removal, the latter being necessary in view of the high solids mode of activated sludge operation which is used.

Ultrafiltration is the lesser known counterpart of hyperfiltration, or reverse osmosis, a process of increasing interest for desalination applications. Ultrafiltration by definition removes only solids and no inorganic salts. Although it requires a sophisticated hydrodynamic system similar to that of RO, it is operated under a much lower pressure, usually about 50 psi versus the 400-1500 psi required for RO. Like RO, it has a problem with membrane flux decline, but this is usually controlled by routine hydrodynamic cleaning techniques. Since ultrafiltration is presently more expensive than settling or filtration, its principal current application is in situations such as small Advanced Waste Treatment plants where space is important, and where the product quality and consistency of supply is vital.

The IOPOR System to be discussed is currently located on the top of Pikes Peak (14,110 ft) in Colorado, and is thus perhaps the world's highest sewage treatment plant. As with the case of Alaska, Pikes Peak is a remote site where pollution hazards in the water-shed are great and where water supply is likewise a difficult matter. (See Plate 2). The wastes are generated largely by the tourist facilities on the Peak. (See Figure 7)

The IOPOR unit was tested for several months at Colorado Springs, during which time mechanical difficulties were corrected. (See Plate 3). A summary of results for the preliminary testing are given in Table 6. Raw sewage from the city was used as a feed. The unit performed extremely and consistently well under a very heavy loading in every respect except perhaps color. Effluent organics were generally of tertiary quality and even the odor was minimal. Frequency distributions for influent and effluent COD are shown in Figure 8; effluent COD was always better than secondary quality.

The IOPOR unit was moved to Pikes Peak in August 1970 as soon as necessary site construction was completed. Membrane modules and plastic parts were removed with the onset of winter in late September, when the Peak facilities and roads were closed. In the meantime, about 3 weeks of operation was completed which included some recycling experience but no direct reuse. Operation with full reuse will commence next summer. A summary of results for operation on the Peak is given in Table 7.

Operation was generally good as in the preliminary trial, even though the waste was somewhat different. The Peak waste has a higher proportion of human wastes than normal municipal waste. Color was again on the high side, but not necessarily a problem. It may be that a small amount of powdered carbon will improve the color. Phosphorus removal was typical of biological treatment. Physical-chemical treatment plants would be superior in this respect if phosphorus were of concern here. However, it is possible that phosphorus removal, if desired, could be improved by adding a precipitant to the aerator. COD and turbidity frequency distributions are shown in Figures 9 and 10. Not much variation is evident for either of them, illustrating that both consistent waste strength and consistent plant performance can probably be expected.

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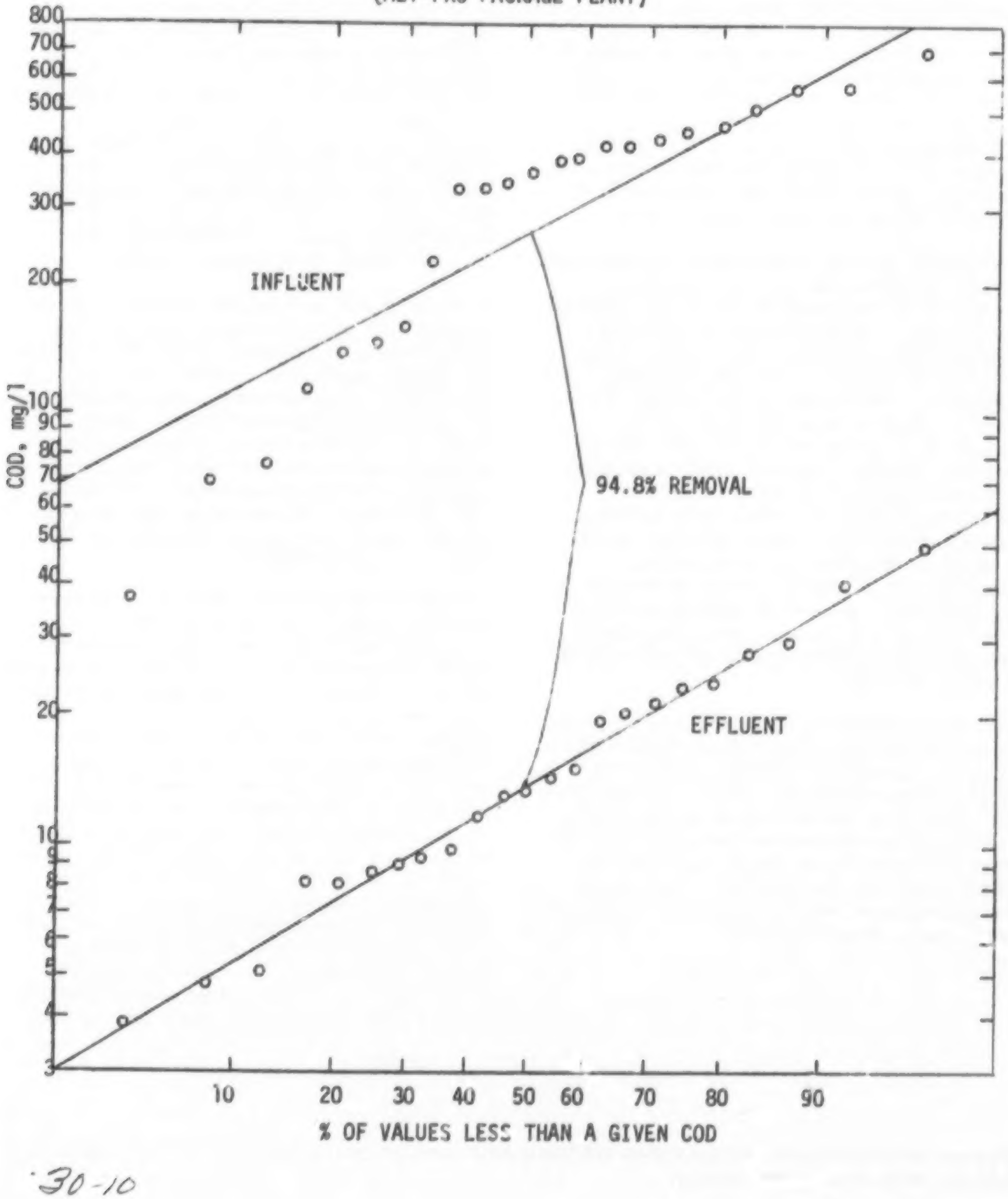
*Mention of commercial products does not imply endorsement by the Office of Water Programs, Environmental Protection Agency.

FIGURE 4

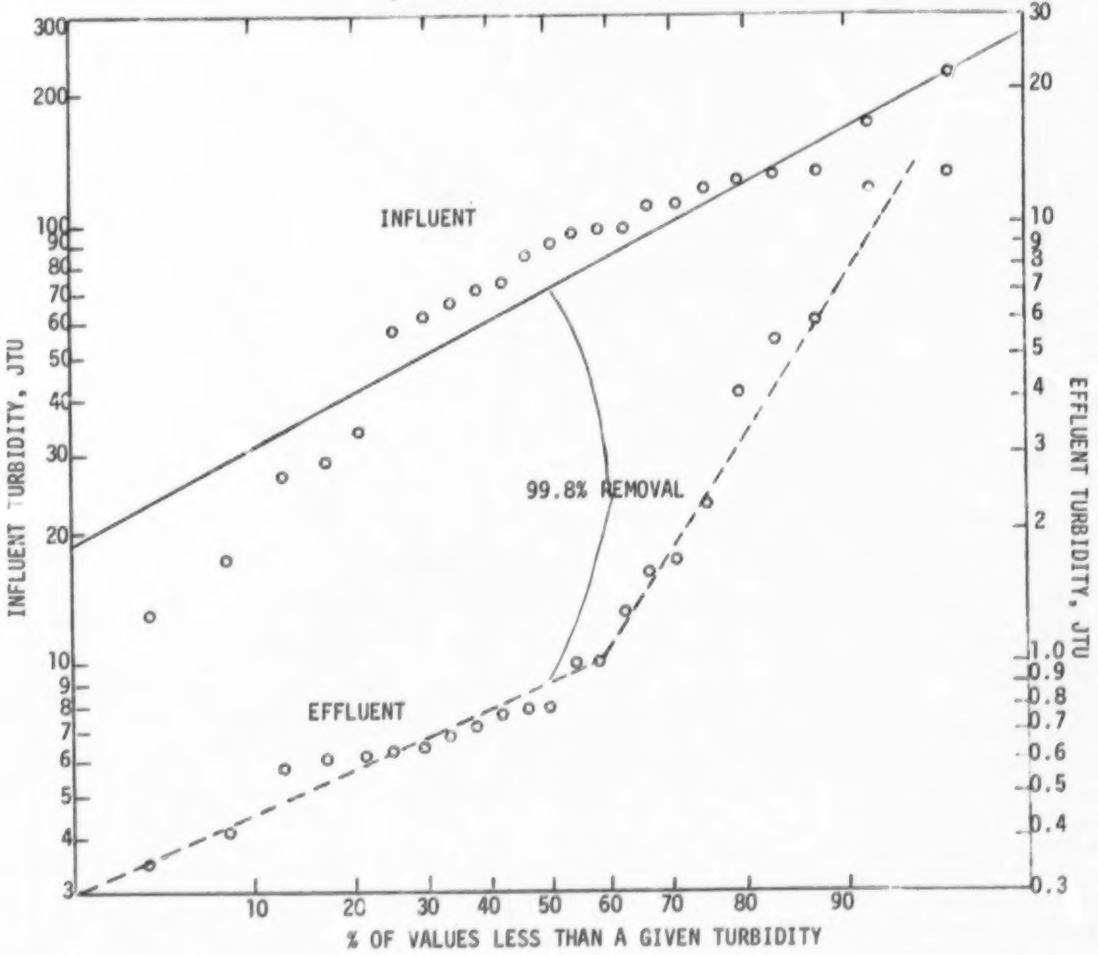
DISTRIBUTION OF INFLUENT & EFFLUENT COD (MET-PRO PACKAGE PLANT)



30-10

FIGURE 5

DISTRIBUTION OF INFLUENT & EFFLUENT TURBIDITY
(MET-PRO PACKAGE PLANT)



from Table 2

$$1 - \frac{L-y}{L} = 1 - 10^{-kt} \qquad (4)$$

multiplying both sides of equation (4) by L:

$$L\left(1 - \frac{(L-y)}{L}\right) = L(1 - 10^{-kt})$$

rearranging and cancelling gives:

$$y = L(1 - 10^{-kt}) \qquad (5)$$

This is the usual form of the BOD equation. To avoid confusion with other "k" values, the deoxygenation rate is usually written as k_1 and the equation becomes.

$$y = L(1 - 10^{-k_1 t}) \qquad (6)$$

The components in Figure 5 are as in III where L is the ultimate oxygen demand at infinite time and y refers to the demand satisfied at time t. The term k_1 refers to a "velocity constant" in physical chemistry terminology. Section II B3 indicates factors that result in system changes during progression of the BOD test that may affect the value of k_1. For this reason the term "rate coefficient" is used for k_1 to recognize that k_1 may not be a "constant" except for limited time periods. As given, k_1 is an expression of the slope dL/dt as a log and is related to the rate of oxidation.

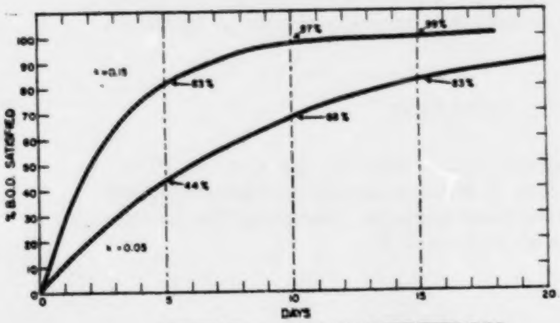
The L value is a laboratory number regarded as a theoretical rather than an actual limit. The limit is useful for an estimation of the effects of a waste upon the receiving water where the total demand is more valid than a part of it as for example a 5 day BOD.

IV SIGNIFICANCE OF BOD CONSTANTS

A The effect of k_1 upon y is shown in Figure 4.

The upper curve represents the BOD of a domestic sewage. The k_1 is 0.15. At this rate, 50% of the demand will be exerted in the first two days, indicating that the organic matter is readily available as food for the organisms. In five days, 83% of the demand has been satisfied and in 15 days, the oxidation is essentially complete.

The lower curve represents the BOD of a relatively stable sample. The k_1 in this case is 0.05. In five days only 44% of the demand is satisfied and at 15 days, there is still 17% of the material unoxidized. Note that at the lower rate, it takes 15 days to accomplish 83% oxidation, while at the higher rate, the same percentage can be accomplished in 5 days.



EFFECT OF k RATE ON SHORT TERM B.O.D.

Figure 4

Laboratory tests on the BOD of waste materials are generally 5-day tests. In the case of these two samples, the standard 5-day interval would represent vastly different degrees of oxidation.

V LOG OF % BOD REMAINING

Using the mathematical relationships established above, a second BOD equation can be developed.

From Table 2:

$$\frac{L - y}{L} = 10^{-k_1 t} = \text{fraction remaining}$$

$$10^{-k_1 t} \times 100 = \%\ \text{remaining}$$

$$\log_{10} (10^{-k_1 t} \times 100) = \log_{10} \%\ \text{remaining}$$

further:

$$\log_{10} (10^{-k_1 t} \times 100) = 2 - k_1 t$$

then:

$$\text{log of \% BOD remaining} = 2 - k_1 t \quad (7)$$

VI SUMMARY

The relationships presented herein form the basis for development of engineering estimates from laboratory data. Validity of the estimate depends upon sampling, prompt and correct BOD technique, judicious data analysis, and realization that the laboratory BOD test does not include many factors controlling stream behavior.

Two examples of the estimation of k and L values are presented in Part 2, which begins on the next page.

ACKNOWLEDGEMENT:

Certain portions of this outline contain materials made available by D. G. Ballinger, F. P. Nixon and D. E. Baumgartner.

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This outline was prepared by F. J. Ludzack, Chemist, National Training Center, DTTB, MDS, WPO, EPA, Cincinnati, OH 45268.

MATHEMATICAL BASIS OF THE BIOCHEMICAL OXYGEN DEMAND (BOD) TEST

ESTIMATION OF k and L

Part 2

I Several methods are available that may give a fair estimate of k_1 and L providing that the observed data plots in a form that suggests a first order reaction rate fit. The fact that stream samples frequently consist of partially stabilized river water mixed with varying amounts of more recent wastewater additions leads to numerous situations where observed data calculated as "a" first order reaction does not give a good fit of observed and calculated data. The low rate oxidation of the aged material and high rate oxidation of the new material simply cannot be explained in terms of one k_1 and L.

The BOD test is not precise enough to distinguish the infinite number of individual rate systems included in deoxygenation of a mixed wastewater by the mixed organisms involved. The persistence of the one first order reaction rate concept (incorrectly called a monomolecular rate) partially is due to the practical limitations of the test. High assimilative oxidation rates generally have been partially completed in the sewer, during compositing or sample storage before BOD analysis, or in the receiving water. Remaining deoxygenation may take the form characteristic of cell mass and storage products, (endogenous oxidation) which for a few days shows a k_1 of about 0.1. If the observation period was extended beyond the usual 7 to 10 days for rate estimation a progressive change of k_1 would become apparent as the more oxidizable components disappear and relatively inert biological or other residues became a larger and larger fraction of the total oxidizable mass. The increased impoundment of surface water makes long-term deoxygenation more and more significant.

The computed k_1 and L are a result of the selected measurement routine, past history of the sample, and the manner of processing the result. The validity of the estimate depends upon engineering judgment and a realization of the variables and effects involved. No two individuals will derive precisely the same values from given data but common sense approaches using mathematics as a tool rather than as a deity, will produce useful estimates for resolution of the problem.

II Useful methods of deriving k_1 include the least squares method of Reed and Theriault (Public Health Bulletin 127, 1927); the Thomas Slope Method (Sew. Works J. 9, No. 3, 425, 1937), the Moments Method of Moore, Thomas, and Snow (Sew. and Ind. Wastes 22, No. 10, 1343, 1950) and the Rapid Ratio Method of Sheehy (JWPCF 32, No. 6, 646, 1960). The first three of these presume a singe rate coefficient and do not give a good fit of data when deoxygenation fails to follow the pattern. Certain other factors enter the picture even when the curve apparently follows first order characteristics (Ludzack et al, Sew. and Ind. Wastes 25, No. 8, 875, 1953). Sheehy's procedure elucidates the disappearance of high rate components during early stages and can be very useful for rapid calculations.

The daily difference method outlined by Tsivoglou (Oxygen Relations in Streams, SEC Tech. Report W-58-2, p. 151, 1958) is an adaptation of Fair and of Velz methods and gives a graphic picture of observed data and predominant rate changes with time. The method is rapid, versatile, and gives a great deal of information in a simple package that is readily assembled. This technique was used to illustrate its applicability as "one" means of estimation.

A Using the data given in Table 1, Part 1.

1 Plot y vs. t on cartisian coordinate paper. Draw a curve of best fit through the observed points, including lags, plateaus, if any, to get a picture of the deoxygenation curve. If a majority of observed values describe a smooth

progression, those that fail to fit may be considered erratic and curve values may be used for subsequent operations. Lags should be eliminated by curve fitting and taking the observed points after the lag termination. (Figure 2)

2 Plot the daily differences, corrected if necessary, on semilog paper with time on the linear scale and the daily difference on the log scale. The differences are conventionally plotted as 1/2, 1-1/2, 2-1/2 days, etc. to illustrate intervals rather than points. (Figure 5)

3 Examination of Figure 2 shows identical daily differences for the last 3 days or $k_1 = 0$ for that interval in Figure 5. That is unlikely considering the short period of observation and the results of the first 6 days.

4 It may be assumed that deoxygenation follows a smooth curve after considering possible lag periods or multicomponent rates operating in combination or sequentially. Daily differences, therefore, should be calculated from a line of best fit such as Figure 2 rather than from the individual points included in Table 1 which may be affected by experimental error.

5 Figure 5 is a plot of the daily differences from Table 1 on the $\log_{10}$ scale vs time on the arithmetic scale. The corrected curve of best fit was not used here to show the effects of the last 3 points on the logarithmic pattern. The slope of the line was well defined on the basis of the first 7 points. Note that the daily differences are plotted at the middle of the time interval, i.e., the deoxygenation occurring from 0 to 1 day appears at the 1/2 day position and that occurring during the second day appears at the 1-1/2 day position.

6 It is advisable to check arithmetic on the work sheet by comparing the sum of the daily differences in Table 1 with that resulting from the line of best fit in Figure 5. In Table 1: $1.8 + 1.6 + 1.2 + \ldots + 0.3 = 8.3$; in Figure 5; $1.88 + 1.50 + 1.20 + \ldots + 0.26 = 8.4$. Since the difference in sums is 1 part in 84 it is apparent that serious errors did not occur in arithmetic or plotting.

7 From Figure 5, the number at the zero intercept of the daily difference slope is a function of L. Other intercepts are a function of L_t using equivalents in Table 2. The number representing L at 0 time = 2.1; the number representing L_t when t = 10 is 0.23. The percent BOD remaining when t = 10 is $L_t/L \times 100$ or

$$\frac{0.23 \times 100}{2.1} = 10.9 \text{ or } 11\%.$$

8 From equation 7:

Log_{10} of the % BOD remaining $= 2 - k_1 t$

The Log_{10} of 11% = 1.04 and t = 10
then $1.04 = 2 - k_1 \times 10$

or $k_1 = 2 - 1.04/10 = \frac{0.96}{10} = 0.096$ or 0.10

9 From equation 6:

$$y_t = L\,(1 - 10^{-k_1 t}) = L\,(1 - \frac{L_t}{L})$$

From Table 1, $y_{10} = 8.3$, and

$(1 - \frac{L_t}{L}) = 0.89$ (Step 7)

The estimate of L becomes

$y_{10} = L\,(1 - \frac{L_t}{L})$ or $8.3 = L\,(0.89)$

$$L = \frac{8.3}{0.89} = 9.34 \text{ or } 9.3 \text{ mg BOD/l.}$$

10 The laboratory test gives estimates of the rate coefficient or k_1 of 0.10 and of L or the Ultimate Oxygen Demand of 9.3 mg of BOD per liter of sample. The data approximates a system consisting primarily of the oxidation of partially stabilized cell mass and storage products and plots as a one rate system during the observation period.

Equations 6 and 7 provide the fundamental relationships and the equivalents in Table 2 may be read from Figure 5.

B The data in Table 3 present a different situation involving more recent contamination.

Table 3

days	BOD	per day
1	2.24	2.24
2	3.18	0.94
3	3.81	0.63
4	4.22	0.41
5	4.56	0.34
6	4.88	0.32
7	5.12	0.24
8	5.32	0.20
9	5.49	0.17
10	5.61	0.12

1 The line of best fit of the observed BODs in Table 3 are shown as a smooth curve in Figure 6.

2 Figure 7 shows the daily differences on the semi log scale vs the time interval on the arithmetic scale. The line ab is a reasonable fit for the slope described by 5 of the 7 daily differences after the 3rd day. It is apparent that the curve in Figure 6 cannot be described as one first order reaction.

The differences among the first 3 observed daily differences and the line ab are 1.55, 0.36 and 0.14 from Figure 7. If the differences are plotted on Figure 7, (coded as x) a new rate cd can be estimated that gives a reasonable fit with 2 of the 3 intervals. The first daily difference is above the slope cd suggesting a 3rd rate group higher than ab or cd. Since this would be based upon a single point in 1 series, in which some discrepancy is apparent in Figure 7 with respect to line fitting, it is advisable to regard it as a possibility as shown by the graphic but withhold judgement on the 3rd rate group for further evidence. The curve in Figure 6 may be approximated by a two rate system operating simultaneously with one of the two nearly completed in 3 days.

3 Mathematically this situation may be expressed as:

$$Yt = L_{cd}(1 - 10^{-k_{cd}t}) + L_{ab}(1 - 10^{-k_{ab}t}) \text{ or}$$

$$= L_{cd}\left(1 - \frac{L_t}{L_{cd}}\right) + L_{ab}\left(1 - \frac{L_t}{L_{ab}}\right)$$

where $\frac{L_t}{L}$ may be obtained from Figure 7 at the designated time intervals for each slope.

4 From Figure 7 the zero and 10 day intercepts of line ab are 0.75 and 0.13.

The $\% \frac{L_t}{L} = \frac{0.13 \times 100}{0.75} = 17.4\%$ BOD remaining when $t = 10$.

The $\log_{10}$ of 17.4 is 1.24.

If the $\log_{10}$ of the % BOD remaining = $2 - k_1 t$

then, $1.24 = 2 - k_{ab} \times 10$ and $k_{ab} =$

$$\frac{2 - 1.24}{10} = \frac{0.76}{10} = 0.076$$

5 From Figure 7 the zero and 2 day intercepts of line cd are 1.40 and 0.22.

$\% \frac{L_t}{L_{cd}} = \frac{0.22 \times 100}{1.40} = 15.7\%$ BOD remaining when t = 2. The $\log_{10}$ of 15.7 is 1.20 as in Step 3:

$$k_{cd} = \frac{2 - 1.20}{2} = \frac{0.80}{2} = 0.40$$

6 From the relation in B2, L_{cd} may be approximated by substituting the observed value for the 2 day BOD in Table 2 or 3.18. The fraction of $\frac{L_t}{L_{ab}}$ from zero to 2 days is $\frac{0.53}{0.75}$ or 0.71 and $(1 - \frac{L_t}{L_{ab}}) = 0.29$, therefore the use of the 2 day observed value for line cd is incorrect because 0.29 L_{ab} is included in the observed value. Since L_{ab} is unknown, the first estimate of L_{cd} will be incorrect by the value of 0.29 L_{ab} but may be approximated later.

If $Y_{2cd} = L_{cd}(1 - \frac{L_t}{L_{cd}})$ where $Y_2 = 3.18$ and $\frac{L_t}{L_{cd}} = \frac{0.22}{1.40}$ then a high approximation of L_{cd} becomes:

$$3.18 = L_{cd} \times 0.84$$

$L_{cd} = \frac{3.18}{0.84}$ or 3.8 mg BOD/l.

7 A similar approximation of L_{ab} may be set up for t = 10 where the observed Y_{10} from Table 2 of 5.6 is corrected by substracting L_{cd} which should be almost complete by 10 days. Y_{10ab} becomes 5.6 - 3.8 = 1.8 and $\frac{L_t}{L} = \frac{0.13}{0.75}$ or 0.174.

Substituting the appropriate numbers as in step 5:

$L_{ab} = \frac{1.8}{0.826} = 2.18$ or 2.2 mg/l.

8 A better approximation of L_{cd} is now possible assuming that the 2 day observed value included the following:

$Y_2 = 3.18 - 0.29 \times 2.2$ or $3.18 - 0.84 = 2.34$

and

$L_{cd} = \frac{2.34}{0.84} = 2.9$ mg BOD/l instead of 3.8

A second approximation of L_{ab} would raise the estimate of L_{ab} because $Y_{10ab} = 5.6 - 2.9 = 2.7$ and

$L_{ab} = \frac{2.7}{0.826} = 3.28$ or 3.3 mg BOD/l and an estimate of the L values of the sample plotted in Figure 6 would be 2.9 + 3.3 or 6.2 mg BOD/ liter.

C The substitution of the derived values for the appropriate and ultimate oxygen demand into the expression given in B2 should give values comparable to the observed BODs in Table 3 or Figure 6. Further, it should be possible to approximate curves for the individual rate systems to obtain daily vectors, the sum of which would compare with the observed points. For example:

$$Y_t = L_{cd}(1 - 10^{-k_{cd}t}) + L_{ab}(1 - 10^{-k_{ab}t})$$

Where $L_{cd} = 2.9$ and $k_{cd} = 0.40$

$L_{ab} = 3.3$ and $k_{ab} = 0.076$

and $10^{-k_1 t}$ may be approximated by $\frac{L_t}{L}$ from Figure 7. (See Table 2)

1 $Y_1 = 2.9\,(1 - \frac{0.56}{1.40}) + 3.3\,(1 - \frac{0.63}{0.75})$

$= 2.9 \times 0.60 + 3.3 \times 0.16$

$= 1.74 + 0.53 = 2.27.$ observed = 2.24

2 $Y_2 = 2.9\,(1 - \frac{0.22}{1.40}) + 3.3\,(1 - \frac{0.53}{0.75})$

$= 2.4 + 0.9 = 3.3$ observed = 3.18

3 $Y_3 = 2.9\,(1 - \frac{<0.01}{1.40}) + 3.3\,(1 - \frac{0.44}{0.75})$

$= 2.9 + 1.3 = 4.2$ observed = 3.81

4 $Y_5 = 2.9 + 3.3\,(1 - \frac{0.31}{0.75})$

$2.9 + 1.9 = 4.8$ observed 4.56

5 $Y_{10} = 2.9 + 3.3\,(1 - \frac{0.13}{0.75})$

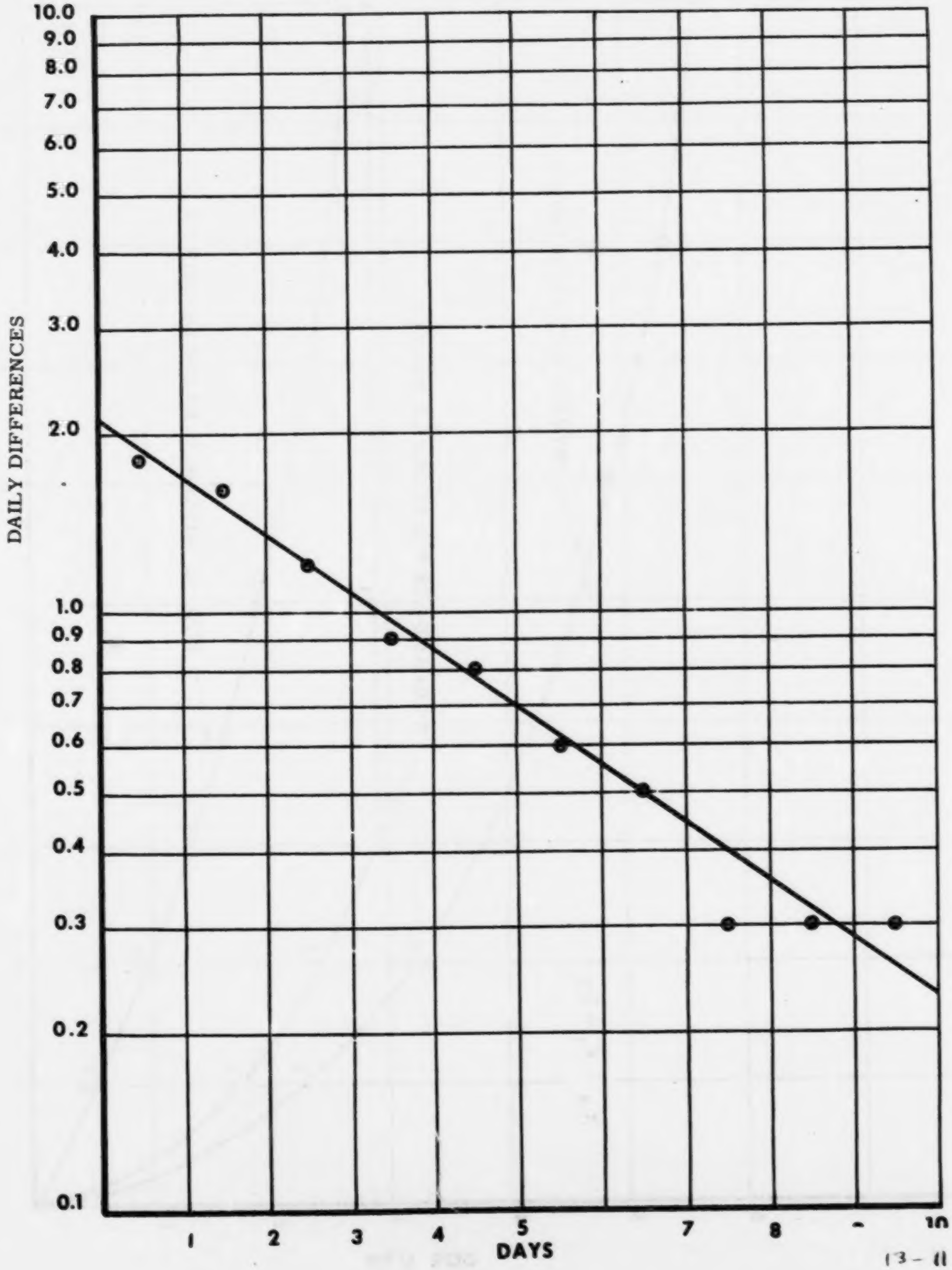
$= 2.9 + 2.7 = 5.6$ observed 5.61

6 These data show a reasonable approximation of the observed BODs by a reverse calculation from the derived rate and ultimate BOD obtained from them. The agreement indicates that approximations made were reasonably correct and that the composite BOD curve in Figure 6 may be described as a 2 rate system as indicated by the BODs in Figure 6. The largest error occurred in calculation of the components for Y_3 at the point in time where the higher rate system was being phased out. Curve fitting, approximations of correction factors for estimation of L, plotting, slide rule and other errors contribute to estimates of k_1 and L in addition to the errors related to the BOD test.

An approximation of k_1 is possible from 2 BOD values obtained at different intervals of time by using the data presented in the Theriault Tables or that given nomographically by the chart on the Rates of BOD Satisfaction.

This outline was prepared by F. J. Ludzack, Chemist, National Training Center, DTTB, MDS, , EPA, Cincinnati, OH 45268.

Figure 5. Log$_{10}$ Slope of the Daily Differences from Figure 2



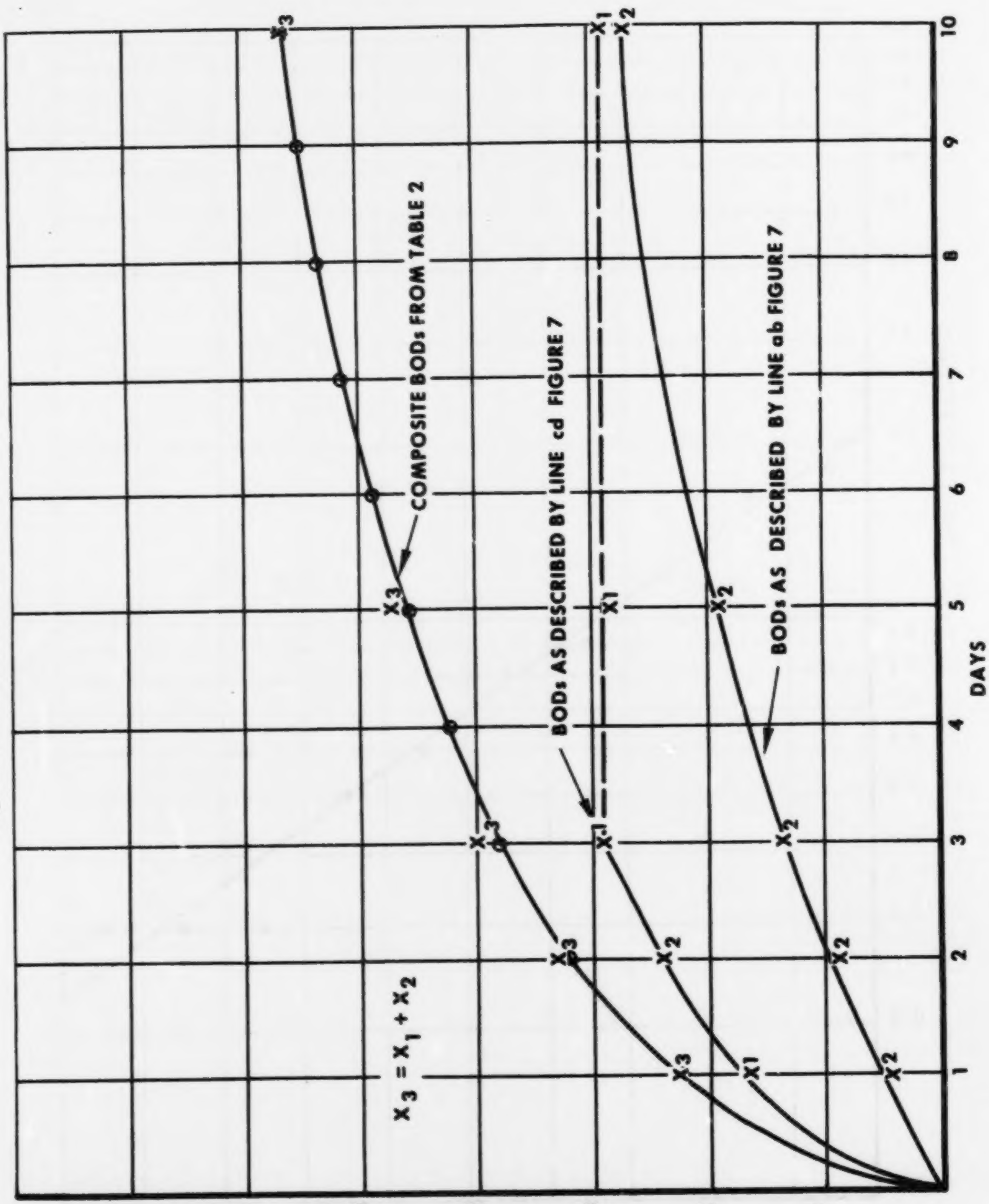
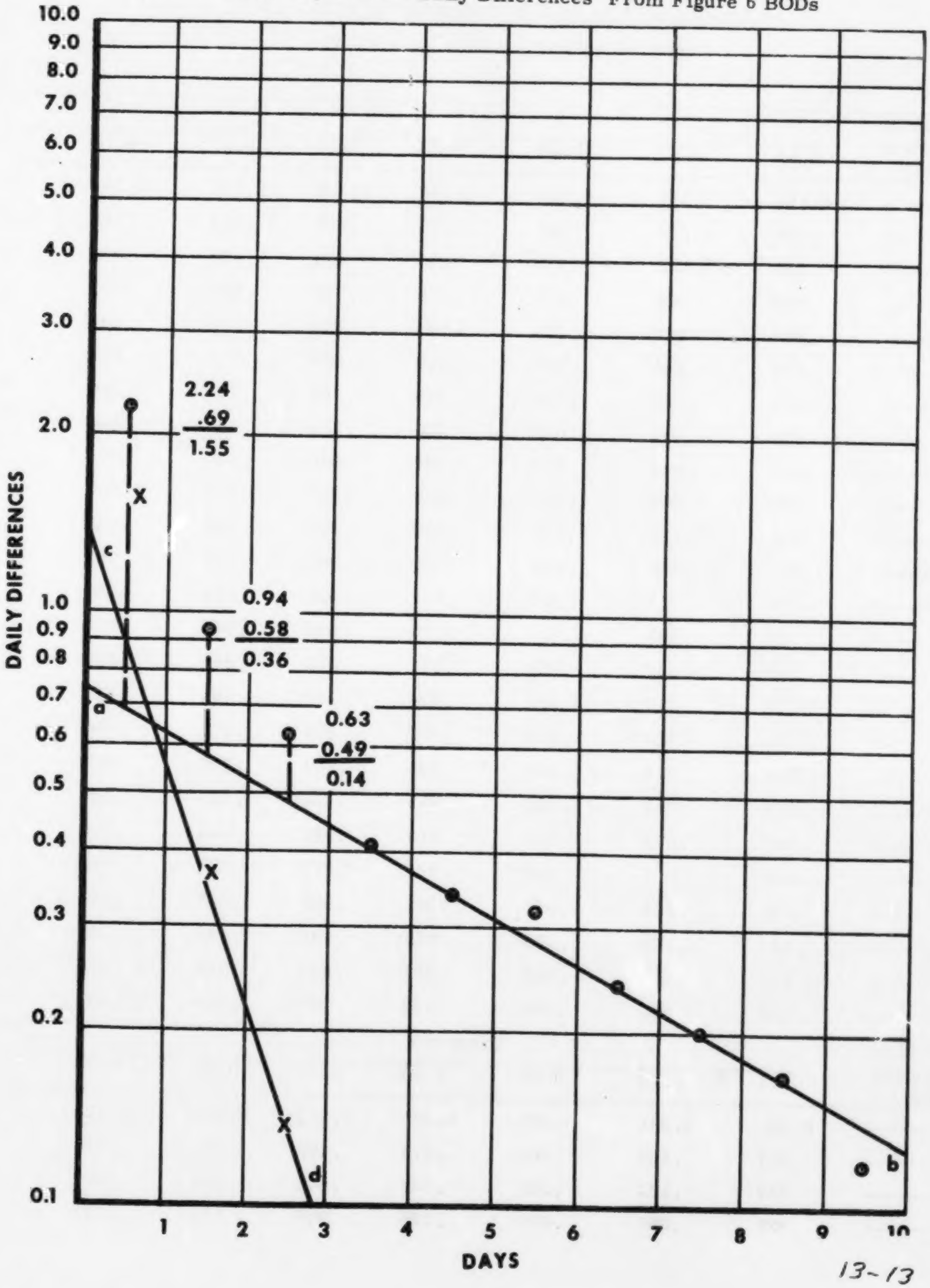


Figure 6. Σ BOD of the Data from Table 2.

Figure 7. Log_{10} Slopes of the Daily Differences From Figure 6 BODs



Theriault Table

NUMERICAL VALUES OF THE FUNCTION (1 - 10^{-kt}) FOR THE RANGE k = 0.040 to k = 0.250

Period of incubation (days)	Value of k						
	0.04	0.05	0.06	0.07	0.08	0.09	0.10
1--------	0.088	0.109	0.129	0.149	0.168	0.187	0.206
2--------	.168	0.206	.241	.276	.308	.339	.369
3--------	.241	0.292	.339	.383	.425	.463	.499
4--------	.308	.369	.425	.475	.521	.563	.602
5--------	.369	.438	.499	.553	.602	.645	.684
6--------	.425	.499	.563	.620	.669	.712	.749
7--------	.475	.553	.620	.676	.725	.766	.800
8--------	.521	.602	.669	.725	.771	.809	.842
9--------	.563	.645	.712	.766	.809	.845	.874
10--------	.602	.684	.749	.800	.842	.874	.900
11--------	.637	.718	.781	.830	.868	.898	.921
12--------	.669	.749	.809	.855	.890	.917	.937
13--------	.698	.776	.834	.877	.909	.932	.950
14--------	.725	.800	.855	.895	.924	.945	.960
15--------	.749	.822	.874	.911	.937	.955	.968
16--------	.771	.842	.890	.924	.948	.964	.975
17--------	.791	.859	.905	.935	.956	.970	.980
18--------	.809	.874	.917	.945	.964	.976	.984
19--------	.826	.888	.928	.953	.970	.981	.987
20--------	.842	.900	.937	.960	.975	.984	.990
21--------	.855	.911	.945	.966	.979	.987	.992
22--------	.868	.921	.952	.971	.983	.990	.994
23--------	.880	.929	.958	.975	.986	.991	.995
24--------	.890	.937	.964	.979	.988	.993	.996
25--------	.900	.944	.968	.982	.990	.994	.997

Period of incubation (days)	Value of k						
	0.11	0.12	0.13	0.14	0.15	0.16	0.17
1--------	0.224	0.241	0.259	0.276	0.292	0.308	0.324
2--------	.397	.425	.450	.475	.499	.521	.543
3--------	.532	.563	.593	.620	.645	.669	.691
4--------	.637	.669	.699	.725	.749	.771	.791

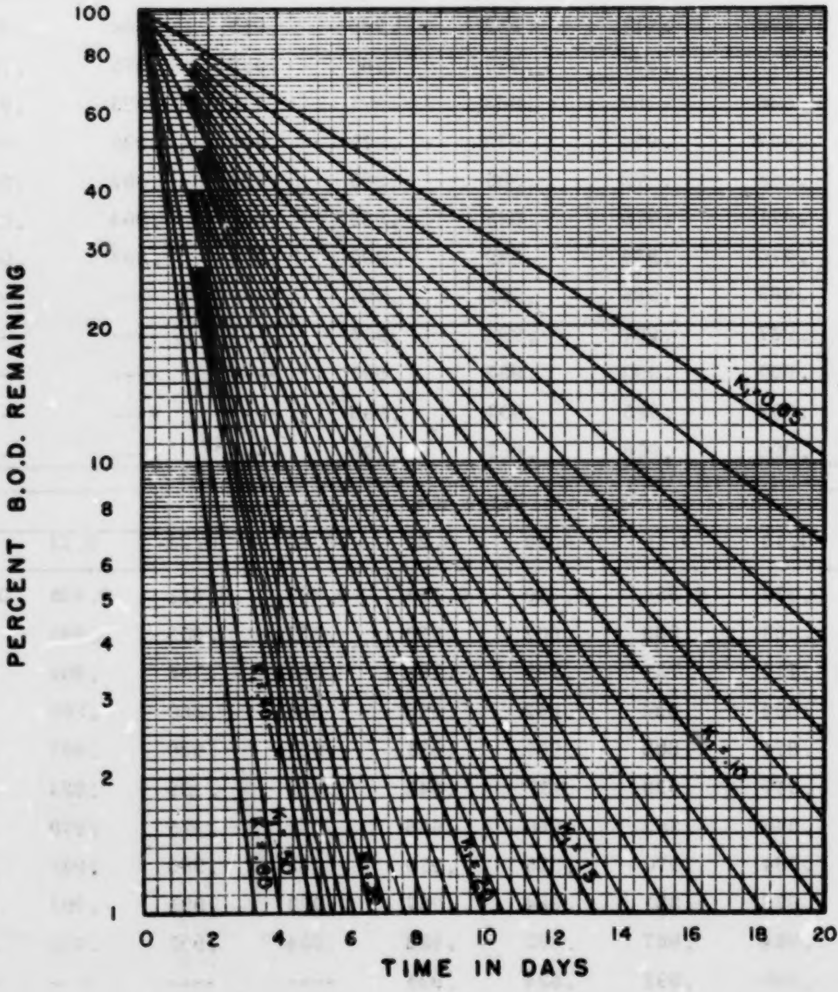
Theriault Table

Period of incubation (days)	Value of k						
	0.11	0.12	0.13	0.14	0.15	0.16	0.17
5--------	.718	.749	.776	.800	.822	.842	.859
6--------	.781	.809	.834	.855	.874	.890	.905
7--------	.830	.855	.877	.895	.911	.924	.935
8--------	.868	.890	.909	.924	.937	.948	.956
9--------	.898	.917	.932	.945	.955	.964	.970
10--------	.921	.937	.950	.960	.968	.975	.980
11--------	.938	.952	.963	.971	.978	.983	.987
12--------	.952	.964	.972	.979	.984	.988	.991
13--------	.963	.972	.980	.985	.989	.992	.994
14--------	.971	.979	.985	.989	.992	.994	.996
15--------	.978	.984	.989	.992	.994	.996	.997
16--------	.983	.988	.992	.994	----	----	----
17--------	.987	.991	.994	.996	----	----	----
18--------	.990	.993	.995	.997	----	----	----
19--------	.992	.995	.997	.998	----	----	----
20--------	.994	.996	.997	.998	----	----	----

Period of incubation (days)	Value of k							
	0.18	0.19	0.20	0.21	0.22	0.23	0.24	0.25
1--------	0.339	0.354	0.369	0.383	0.397	0.411	0.425	0.438
2--------	.563	.583	.602	.620	.637	.653	.669	.684
3--------	.712	.731	.749	.766	.781	.796	.809	.822
4--------	.809	.826	.842	.855	.868	.880	.890	.900
5--------	.874	.888	.900	.911	.921	.929	.937	.944
6--------	.917	.928	.937	.945	.952	.958	.934	.968
7--------	.945	.953	.960	.966	.971	.975	.979	.982
8--------	.964	.970	.975	.979	.983	.986	.988	.990
9--------	.976	.981	.984	.987	.990	.991	.993	.994
10--------	.984	.987	.990	.992	.994	.995	.996	.997
11--------	.990	.992	.994	.995	----	----	----	----
12--------	.993	.995	.996	.997	----	----	----	----
13--------	.995	.997	.997	.998	----	----	----	----
14--------	.997	.998	.998	.999	----	----	----	----
15--------	.998	.999	.999	.999	----	----	----	----

RATES OF B.O.D. SATISFACTION

FOR VALUES OF K_1 FROM .05 TO.60



13-16

CHEMICAL OXYGEN DEMAND AND COD/BOD RELATIONSHIPS

I DEFINITION

A The Chemical Oxygen Demand (COD) is an estimate of the proportion of the sample matter susceptible to oxidation by a strong chemical oxidant. The current edition of Standard Methods,(2) specifies organic material which is generally the situation but not necessarily applicable.

B A variety of terms have been and are used for the test described here as COD:

1 Oxygen absorbed (OA) primarily in British practice.

2 Oxygen consumed (OC) preferred by some, but unpopular.

3 Chemical oxygen demand (COD) current preference.

4 Complete oxygen demand (COD) misnomer.

5 Dichromate oxygen demand (DOC) earlier distinction of the current preference for COD by dichromate or a specified analysis such as Standard Methods.

6 Others have been and are being used. Since 1960, terms have been generally agreed upon within most professional groups as indicated in I-A and B-3 and the explanation in B-5.

C The concept of the COD is almost as old as the BOD. Many oxidants and variations in procedure have been proposed, but none have been completely satisfactory.

1 Ceric sulfate has been investigated, but in general it is not a strong oxidant.

2 Potassium permanganate was one of the earliest oxidants proposed and until recently appeared in Standard Methods (9th ed.) as a standard procedure. It is currently used in British practice as a 4-hr. test at room temperature.

a The results obtained with permanganate were dependent upon concentration of reagent, time of oxidation, temperature, etc., so that results were not reproducible.

3 Potassium iodate or iodic acid is an excellent oxidant but methods employing this reaction are time-consuming and require a very close control.

4 A number of investigators have used potassium dichromate under a variety of conditions. The method proposed by Moore at SEC is the basis of the standard procedure.(1, 2) Statistical comparisons with other methods are described.(3)

5 Effective determination of elemental carbon in wastewater was sought by Buswell as a water quality criteria.

a Van Slyke(4) described a carbon determination based on anhydrous samples and mixed oxidizing agents including sulfuric, chromic, iodic and phosphoric acids to obtain a yield comparable to the theoretical on a wide spectrum of components.

b Van Hall, et al.,(5) used a heated combustion tube with infrared detection to determine carbon quickly and effectively by wet sample injection.

6 Current development shows a trend to instrumental methods automating

conventional procedures or to seek elemental or more specific group determination.

II RELATIONSHIP OF THE COD TEST WITH OTHER OXIDATION CRITERIA IS INDICATED IN TABLE 1.

A Table 1

Test	Test Temp. °C	Reaction time	Oxidation system	Variables
BOD	20	days	Biol. prod. Enz. Oxidn.	Compound, environment, biota, time, numbers. Metabolic acceptability, etc.
COD	145	2 hrs.	50% H_2SO_4 $K_2Cr_2O_7$ May be catalyzed	Susceptibility of the test sample to the specified oxidation
IDOD	20	15'	Diss. oxyg.	Includes materials rapidly oxidized by direct action, Fe^{+2}, SH.
Van Slyke Carbon detn.	400+	1 hr.	H_3PO_4 HIO_3 H_2SO_4 $K_2Cr_2O_7$ Anhydrous	Excellent approach to theoretical oxidation for most compounds (N-nil)
Carbon by combustion +IR	950	minutes	Oxygen atm. catalyzed	Comparable to theoretical for carbon only.
Chlorine Demand	20	20 min.	HOCl soln.	Good NH_3 oxidn. Variable for other compounds.

B From Table 1 it is apparent that oxidation is the only common item of this series of separate tests.

1 Any relationships among COD & BOD or any other tests are fortuitous because the conditions of test tend to give results indicating the susceptibility of a given sample to oxidation under specified conditions that are different for each test.

2 If the sample is primarily composed of compounds that are oxidized by both procedures (BOD and COD) a relationship may be established.

a The COD procedure may be substituted (with proper qualifications) for BOD or the COD may be used as an indication of the dilution required for setting up BOD analysis.

b If the sample is characterized by a predominance of material that can be chemically, but not biochemically oxidized, the COD will be greater than the BOD. Textile wastes, paper mill wastes, and other wastes containing high concentrations of cellulose have a high COD, low BOD.

c If the situation in item b is reversed the BOD will be higher than the COD. Distillery wastes or refinery wastes may have a high BOD, low COD, unless catalyzed by silver sulfate.

d Any relationship established as in 2a will change in response to sample history and environment. The BOD tends to decrease more rapidly than the COD. Biological cell mass or detritus produced by biological action has a low BOD but a relatively high COD. The COD/BOD ratio tends to increase with time, treatment, or conditions favoring stabilization.

III ADVANTAGES AND LIMITATIONS OF THE COD TEST(2) AS RELATED TO BOD

A Advantages

1 Time, manipulation, and equipment costs are lower for the COD test.

2 COD oxidation conditions are effective for a wider spectrum of chemical compounds.

3 COD test conditions can be standardized more readily to give more precise results.

4 COD results are available while the waste is in the plant, not several days later, hence, plant control is facilitated.

5 COD results are useful to indicate downstream damage potential in the form of sludge deposition.

6 The COD result plus the oxygen equivalent for ammonia and organic nitrogen is a good estimate of the ultimate BOD for many municipal wastewaters.

B Limitations

1 Results are not applicable for estimating BOD except as a result of experimental evidence by both methods on a given sample type.

2 Certain compounds are not susceptible to oxidation under COD conditions or are too volatile to remain in the oxidation flask long enough to be oxidized.

Ammonia, aromatic hydrocarbons, saturated hydrocarbons, pyridine, and toluene are examples of materials with a low analytical response in the COD test.

3 Dichromate in hot 50% sulfuric acid requires close control to maintain safety during manipulation.

4 Oxidation of chloride to chlorine is not closely related to BOD but may affect COD results.

5 It is not advisable to expect precise COD results on saline water.

IV BACKGROUND OF THE STANDARD METHODS COD PROCEDURE

A The COD procedure(1) considered dichromate oxidation in 33 and 50 percent sulfuric acid. Results indicated preference of the 50 percent acid concentration for oxidation of sample components. This is the basis for the present standard procedure.

B Muers(6) suggested addition of silver sulfate to catalyze oxidation of certain low molecular weight aliphatic acids and alcohols. The catalyst also improves oxidation of most other organic components to some extent but does not make the COD test universally applicable for all chemical pollutants.

C The unmodified COD test result (A) includes oxidation of chloride to chlorine. Each mg of chloride will have a COD equivalent of 0.23 mg. Chlorides must be determined in the sample and the COD result corrected accordingly.

1 For example, if a sample shows 300 mg of COD per liter and 200 mg Cl^- per liter the corrected COD result will be 300 -(200 x 0.23) or 300 - 46 = 254 mg COD/l on a chloride corrected basis.

2 Silver sulfate addition as a catalyst tends to cause partial precipitation of silver chloride even in the hot acid solution. Chloride corrections are questionable unless the chloride is oxidized before addition of silver sulfate, i.e., reflux for 15 minutes for chloride oxidation, add Ag_2SO_4, and continue the reflux or use of $HgSO_4$ (D).

D Dobbs and Williams(7) proposed prior complexation of chlorides with $HgSO_4$ to prevent chloride oxidation during the test. A ratio of about 10 of Hg^{++} to 1 of Cl^- (wt. basis) appears essential. The Cl^- must be complexed in acid solution before addition of dichromate and silver sulfate.

1 For unexplained reasons the $HgSO_4$ complexation does not completely prevent chloride oxidation in the presence of high chloride concentrations.

2 Factors have been developed to provide some estimate of error in the result due to incomplete control of chloride behavior. These tend to vary with the sample and technique employed.

E It is not likely that COD results will be precise for samples containing high chlorides. Sea water contains 18000 to 21000 mgCl^-/l normally. Equivalent chloride correction for COD exceeds 4000 mg/l. The error in chloride determination may give negative COD results upon application of the correction.

Incomplete control of chloride oxidation with $HgSO_4$ may give equally confusing results.

$HgSO_4$ appears to give precise results for COD when chlorides do not exceed about 2000 mg/l. Interference increases with increasing chlorides at higher levels.

F The 12th edition of Standard Methods reduced the amount of sample and reagents to 40% of amounts utilized in previous editions. There has been no change in the relative proportions in the test. This step was taken to reduce the cost of providing expensive mercury and silver sulfates required. Results are comparable as long as the proportions are identical. Smaller aliquots of sample and reagents require more care during manipulation to promote precision.

G The EPA Methods for COD

1 For routine level COD (samples having an organic carbon concentration greater than 15 mg/liter and a chloride concentration less than 2000 mg/liter), the EPA specifies the procedures found in Standard Methods (2) and in ASTM(8).

2 For low level COD (samples with less than 15 mg/liter organic carbon and chloride concentration less than 2000 mg/liter), EPA provides an analytical procedure (9). The difference from the routine procedure primarily involves a greater sample volume and more dilute solutions of dichromate and ferrous ammonium sulfate.

3 For saline samples (chloride level exceeds 1000 mg/liter and COD is greater than 250 mg/liter), EPA provides an analytical procedure(9) involving preparation of a standard curve of COD versus mg/liter chloride to correct the calculations. Volumes and concentrations for the sample and reagents are adjusted for this type of determination.

V The precision of the unmodified COD result shows a standard deviation of ± 4% of the mean [3] on low chloride samples. Silver sulfate modified COD results are likely to show a standard deviation about twice that without catalysis, due to questionable chloride behavior. The determination of chloride frequently shows a coefficient of variation (s/x) of 10 to 15%, hence high chloride samples result in COD precision controlled more by chloride behavior than organic oxidation.

VI REMARKS PERTINENT TO EFFECTIVE COD DETERMINATIONS INCLUDE:

A Sample size and COD limits for 0.25 N reagents are approximately as given. For 0.025 N reagents multiply COD by 0.1. Use the weak reagents for COD's in the range of 5-50 mg/1, (low level).

Sample Size	mg COD/1
20 ml	2000
10 ml	4000
5 ml	8000

B Most organic materials oxidize relatively rapidly under COD test conditions. A significant fraction of oxidation occurs during the heating upon addition of acid. The color change of dichromate after acid addition indicates the approximate fraction of dichromate remaining. If the mixed sample color changes from yellow to green after acid addition the sample was too large. Discard without reflux and repeat with a smaller aliquot until the color after mixing does not go beyond a brownish hue. The dichromate color change is less rapid with sample components that are slowly oxidized under COD reaction conditions.

C Chloride concentrations should be known for all test samples and results interpreted accordingly.

D Special precautions advisable for the regular COD procedure and essential when using 0.025 N reagents include:

1 Keep the apparatus assembled when not in use.

2 Plug the condenser breather tube with glass wool to minimize dust entrance.

3 Wipe the upper part of the flask and lower part of the condenser with a wet towel before disassembly to minimize sample contamination.

4 Steam out the condenser after use for high concentration samples and periodically for regular samples. Use the regular blank reagent mix and heat, without use of condenser water, to clean the apparatus of residual oxidizable components.

5 Distilled water and sulfuric acid must be of very high quality to maintain low blanks on the refluxed samples for the 0.025 N oxidant.

ACKNOWLEDGEMENT:

Certain portions of this outline contain training material from prior outlines by R. C. Kroner, R. J. Lishka, and J. W. Mandia.

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See Next Page.

This outline was prepared by F. J. Ludzack, Chemist, National Training Center, MDS, WPO, EPA, Cincinnati, OH 45268.

TOTAL CARBON ANALYSIS

I INTRODUCTION

A History of Carbon Analyses

In the wake of a rapid population growth, and the increasing heavy use of our natural waterways, the nation, and indeed the world, is presented with the acute problem of increased pollutional loads on streams, rivers and other receiving bodies. This has resulted in a growing awareness of the need to prevent the pollution of streams, rivers, lakes and even the oceans. Along with this awareness has developed a desire for a more rapid and precise method of detecting and measuring pollution due to organic materials.

B The Methods

In the past, two general approaches have been used in evaluating the degree of organic water pollution.

1 The determination of the amount of oxygen or other oxidants required to react with organic impurities.

2 The determination of the amount of total carbon present in these impurities.

C Oxygen Demand Analyses

The first approach is represented by conventional laboratory tests for determining Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD). One of the principal disadvantages of these tests is that they are limited primarily to historical significance, that is, they tell what a treatment plant had been doing, since they require anywhere from two hours to five days to complete. Since up to now no faster method has been available, traditional BOD and COD determinations have become accepted standards of measure in water pollution control work even though they are essentially ineffective for process control purposes.

Until the introduction of the Carbonaceous Analyzer, all methods taking the second approach, the total carbon method of evaluating water quality, also proved too slow.

II THE ANALYSIS OF CARBON

A Pollution Indicator

Now the carbonaceous analyzer provides a means to determine the total carbon content of a dilute water sample in approximately two minutes. With proper sample preparation to remove inorganic carbonates, the instrument determines the total organic carbon content in the sample.

B Relationship of Carbon Analysis to BOD and COD

This quantity varies with the structure from 27 percent for oxalic acid through 40 percent for glucose to 75 percent for methane. The ratio of COD to mg carbon also varies widely from 0.67 for oxalic acid through 2.67 for glucose to 5.33 for methane. Representative secondary sewage effluents have given a ratio of COD to carbon content of between 2.5 and 3.5 with the general average being 3.0.

The BOD, COD and carbon contents of these and some other representative compounds are summarized in the following table.

Sample	5-Day BOD-mg/mg	COD-mg/mg	% Carbon
Stearic Acid - $C_{18}H_{36}O_2$	.786	2.91	76
Glucose - $C_6H_{12}O_6$	.73	1.07	40
Oxalic Acid - $C_2H_2O_4$	.14	.18	27
Benzoic Acid - $C_7H_6O_2$	1.38	1.97	69
Phenol - C_6H_6O	.05 to 2.1 depending upon concentration	2.36	77
Potassium Acid Phthalate $KHC_8H_4O_4$	.95	1.15	47
Salicylic Acid - $C_7H_6O_3$	1.25	1.60	61
Secondary Effluent, Clarified	13*	75*	21*
" " "	23*	67*	12*
" " "	4*	36*	7*

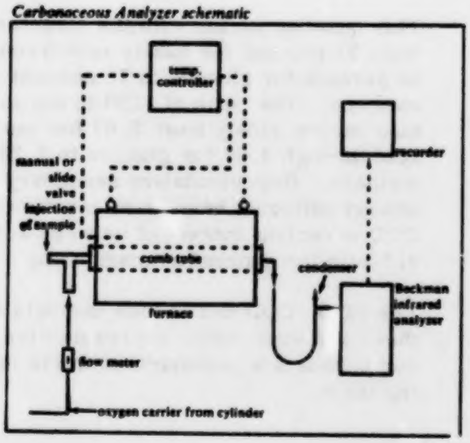
*In units of mg/l

III THE CARBON ANALYZER

A Principle of Operation

Basically the carbonaceous analyzer consists of three sections - a sampling and oxidizing system, a Beckman Model 315 Infrared Analyzer, and a strip-chart recorder.

Carbonaceous Analyzer schematic


temp. controller
recorder
manual or slide valve injection of sample
comb tube
condenser
Beckman infrared analyzer
furnace
flow meter
oxygen carrier from cylinder

A micro sample (20-40 μl) of the water to be analyzed is injected into a catalytic combustion tube which is enclosed by an electric furnace thermostated at 950°C. The water is vaporized and the carbonaceous material is oxidized to carbon dioxide (CO_2) and steam in a carrier stream of pure oxygen. The oxygen flow carries the steam and CO_2 out of the furnace where the steam is condensed and the condensate removed. The CO_2, oxygen and remaining water vapor enter an infrared analyzer sensitized to provide a measure of CO_2. The output of the infrared analyzer is recorded on a strip chart, after which, the curve produced can be evaluated by comparing peak height with a calibration curve based upon standard solutions. Results are obtained directly in milligrams of carbon per liter.

B Application

Results(1) show that the method is applicable for most, if not all, water-soluble organic compounds -- including those that contain sulfur, nitrogen, and volatiles.

Nonvolatile organic substances can be differentiated from volatiles, such as carbon dioxide or light hydrocarbons by determination of carbon both before and after the sample solution has been blown with an inert gas.

C Sample Preparation

The Carbonaceous Analyzer is often referred to as a total carbon analyzer because it provides a measure of all the carbonaceous material in a sample, both organic and inorganic. However, if a measure of organic carbon alone is desired, the inorganic carbon content of the sample can be removed during sample preparation.

1 Removal of inorganic carbon

The simplest procedure for removing inorganic carbon from the sample is one of acidifying and blowing. A few drops of HCl per 100 ml of sample will normally reduce pH to 2 or less, releasing all the inorganic carbon as CO_2. Five minutes of blowing with a gas free of CO_2 sweeps out the CO_2 formed by the inorganic carbon. Only the organic carbon remains in the sample and may be analyzed without the inorganic interference.

2 Volatile carbonaceous material

Volatile carbonaceous material that may be lost by blowing is accounted for by using a dual channel carbon analyzer. Beckman's new analyzer has the previously detailed high temperature (950°C) furnace plus a low temperature (150°C) one. Using quartz chips wetted with phosphoric acid, the low temperature channel senses only the CO_2 (freed by the acid) in the original sample. The remaining organics and water are retained in the condenser connected to this low temperature furnace. None of the organics are oxidized by the 150°C furnace.

By injecting a sample into the low temperature furnace, a peak representing the inorganic carbon is obtained on the strip chart. Injecting a non-acidified sample into the high temperature furnace yields a peak representing the total carbon. The difference between the values determined for the two peaks is the total organic carbon.

3 Dilute samples

If the sample is dilute (less than 100 mg/liter carbon) and is a true solution (no suspended particles) no further preparation is required.

4 Samples containing solids

If the sample contains solids and/or fibers which are to be included in the determination, these must be reduced in size so that they will be able to pass through the needle which has an opening of 170 microns (needles having larger openings may be obtained if necessary). In most cases, mixing the sample in a Waring Blender will reduce the particle size sufficiently for sampling.

IV PROCEDURE FOR ANALYSIS

A Interferences

Water vapor resulting from vaporization of the sample, causes a slight interference in the method. Most of the water is trapped out by the air condenser positioned immediately after the combustion furnace. However, a portion of the water vapor passes through the system into the infrared detector and appears on the strip chart as carbon. The water blank also appears on the standard calibration curve, and is therefore removed from the final calculation. In tests of solutions containing the following anions: NO_3^-, Cl^-, SO_4^{-2}, PO_4^{-3}, no interference was encountered with concentrations up to one percent.

B Precision and Accuracy

The recovery of carbon from standard solutions is 98.5 - 100.0 percent. The minimum detectable concentration using the prescribed operating instructions is 1 mg/l carbon. Generally, the data are reproducible to ± 1 mg/l with a standard deviation of 0.7 mg/l at the 100 mg/l level.

V APPLICATIONS

Several of the many research and industrial applications of the Carbonaceous Analyzer are listed below:

A Determine the efficiency of various wastewater renovation processes, both in the laboratory and in the field.

B Compare a plant's waste outlet with its water inlet to determine the degree of contamination contributed.

C Monitoring a waste stream to check for product loss.

D Follow the rate of utilization of organic nutrients by micro-organisms.

E To detect organic impurities in inorganic compounds.

VI ADVANTAGES OF CARBON ANALYZER

A Speed

The Carbonaceous Analyzer's most important advantage is its speed of analysis. One analysis can be performed in 2-3 minutes. This speed of analysis brings about another advantage, economy of operation. Working with dilute samples, one man can run ten to twenty carbon determinations per hour. This is probably more than the number of COD or BOD tests that can even be started, much less completed, in the same period of time.

B Total Carbon

Another advantage is that the measure of carbon is a total one. The oxidizing system of the analyzer brings about complete oxidation of any form of carbon. No compound has been found to which the method is inapplicable.

VII CONCLUSIONS

The Carbonaceous Analyzer provides a rapid and precise measurement of organic carbon in both liquid and air samples. It should be found useful for many research and industrial applications, a few of which have been mentioned.

Because of its rapidity it may be found more useful than the more time-consuming BOD and COD measurements for monitoring industrial waste streams or waste treatment processes.

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This outline was prepared by Robert T. Williams, Chief, Analytical Applications Laboratory, AWTL, NERC, Cincinnati, OH 45268 and revised by Charles J. Moench, Jr., Waste Identification and Analysis, AWTL, NERC, Cincinnati, OH 45268.

AMMONIA, NITRITES AND NITRATES

I SOURCES AND SIGNIFICANCE OF AMMONIA, NITRITES AND NITRATES IN WATER

The natural occurrence of nitrogen compounds is best demonstrated by the nitrogen cycle (Figure 1).

A Ammonia

1 Occurrence

Ammonia is a product of the microbiological decay of animal and plant protein. In turn, it can be used directly to produce plant protein. Many fertilizers contain ammonia.

2 Significance

The presence of ammonia nitrogen in raw surface waters might indicate domestic pollution. Its presence in waters used for drinking purposes may require the addition of large amounts of chlorine in order to produce a free chlorine residual. The chlorine will first react with ammonia to form chloramines before it exerts its full bactericidal effects (free chlorine residual).

B Nitrites

1 Occurrence

Nitrite nitrogen occurs in water as an intermediate stage in the biological decomposition of organic nitrogen. Nitrite formers (nitrosomonas) convert ammonia under aerobic conditions to nitrites. The bacterial reduction of nitrates can also produce nitrites under anaerobic conditions. Nitrite is used as a corrosion inhibitor in industrial process water.

2 Significance

Nitrites are usually not found in surface water to a great extent. The presence of large quantities indicates a source of wastewater pollution.

C Nitrates

1 Occurrence

Nitrate formers convert nitrites under aerobic conditions to nitrates (nitrobacter). During electrical storms, large amounts of nitrogen (N_2) are oxidized to form nitrates. Finally, nitrates can be found in fertilizers.

2 Significance

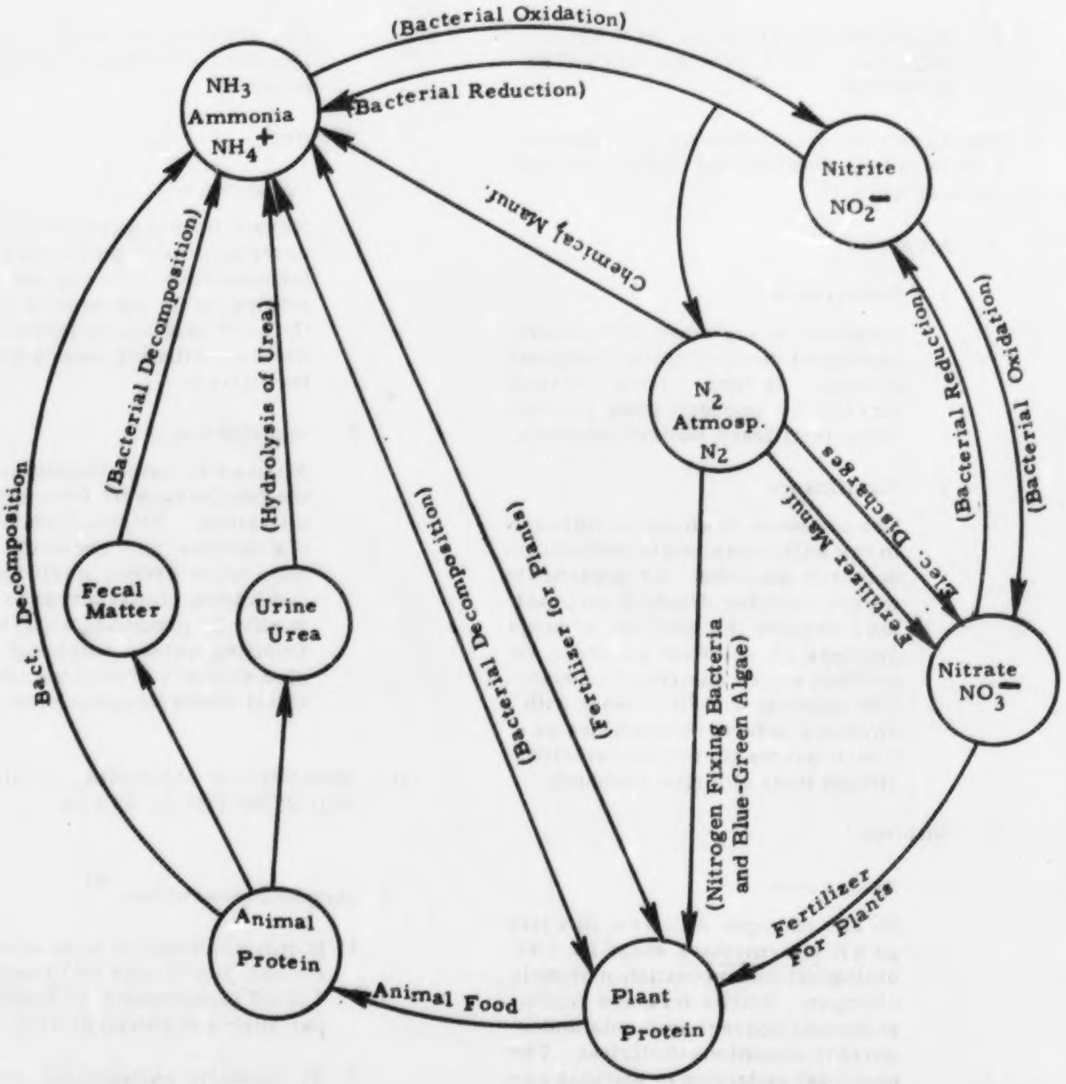
Nitrates in water usually indicate the final stages of biological stabilization. Nitrate rich effluents discharging into receiving waters can, under proper environmental conditions, cause stress to stream quality by producing algal blooms. Drinking water containing excessive amounts of nitrates can cause infant methemoglobinemia.

II ANALYSIS OF AMMONIA, NITRITES AND NITRATES IN WATER

A Sample Preservation (8)

1 If only ammonia is to be determined on the sample, it may be preserved with 1.0 ml of concentrated sulfuric acid per liter and stored at 4° C.

2 To preserve samples for any of the nitrogen procedures, add 40 mg $HgCl_2$ and store at 4° C. Even when so preserved, conversion of organic nitrogen to ammonia may occur. Preserved samples should be analyzed as soon possible.


(Bacterial Oxidation)
NH_3 Ammonia NH_4^+
(Bacterial Reduction)
Nitrite NO_2^-
Chemical Manuf.
N_2 Atmosp. N_2
Elec. Discharges
Fertilizer Manuf
(Bacterial Reduction)
(Bacterial Oxidation)
Nitrate NO_3^-
(Bacterial Decomposition)
(Hydrolysis of Urea)
Bact. Decomposition
Fecal Matter
Urine Urea
(Bacterial Decomposition)
(Fertilizer for Plants)
(Nitrogen Fixing Bacteria and Blue-Green Algae)
Fertilizer For Plants
Animal Protein
Animal Food
Plant Protein

THE NITROGEN CYCLE

Figure 1

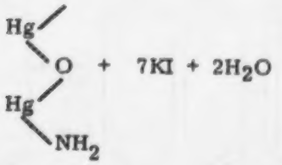
B Determination of Ammonia

1 Nesslerization

a Reaction

Nessler's reagent, a strong alkaline solution of potassium mercuric iodide, combines with NH_3 in alkaline solution to form a yellowish brown colloidal dispersion.

$2K_2HgI_4 + NH_3 + 3KOH \longrightarrow$



$+ 7KI + 2H_2O$

Yellow-Brown

The intensity of the color follows the Beer-Lambert Law and exhibits maximum absorption at 425 nm.

b Interferences

1) Nessler's reagent forms a precipitate with some ions (e.g., Ca^{++}, Mg^{++}, Fe^{+++}, and $S^{=}$). These ions can be eliminated in a pretreatment flocculation step with zinc sulfate and alkali. Also, EDTA or Rochelle salt solution prevents precipitation with Ca^{++} or Mg^{++}.

2) Residual chlorine indicates ammonia may be present in the form of chloramines. The addition of sodium thiosulfate will convert these chloramines to ammonia.

3) Certain organics may produce an off color with Nessler's reagent. If these compounds are not steam distillable, the interference may be eliminated in the distillation method.

4) If the turbidity and natural color of the sample cannot be eliminated with flocculation, it is then necessary to use the following distillation method.

2 Distillation

a Reaction

1) The sample is distilled in the presence of a phosphate buffer at pH 7.2 - 7.4.

$$NH_4 + \xrightarrow{\Delta} NH_3 + H^+$$

$$H^+ + Na_2HPO_4 \longrightarrow NaH_2PO_4 + Na^+$$

Buffer

pH maintained between 7.2 - 7.4

2) The ammonia in the distillate is then measured by either of two techniques.

   a) Nesslerization is used for samples containing less than 1 mg/l of ammonia nitrogen.

   b) Absorption of NH_3 by boric acid and back titration with a standard strong acid is more suitable for samples containing more than 1 mg NH_3 N/l.

$$NH_3 + HBO_2 \longrightarrow NH_4^+ + BO_2^-$$

$$BO_2^- + H^+ \xrightarrow[+]{\text{Methyl Red}} HBO_2$$

Methylene Blue

pH 7.8 - 8.0 Green

pH 6.8 - 7.0 Purple

b Interferences

1) Calcium reacts with the phosphate buffer releasing H^+ and lowering the pH in the distillation step. When the sample contains more than 250 mg Ca^{++}/l, it may be necessary to adjust the pH to 7.4 after adding the buffer.

2) Residual chlorine.

3) Aliphatic and aromatic amines may distill over and cause positive interference by reacting in the acid titration.

3 Precision and Accuracy

On a synthetic sample containing 0.8 mg ammonia nitrogen/l, the ARS Water Nutrients Study (1966) reported results as shown in Table 1.

Method	Standard Deviation	Mean Error
Direct Nesslerization	±0.077 mg/l	0.00 mg/l
Distillation with Nesslerization	±0.100 mg/l	+0.02 mg/l
Distillation with Titration	±0.167 mg/l	+0.04 mg/l

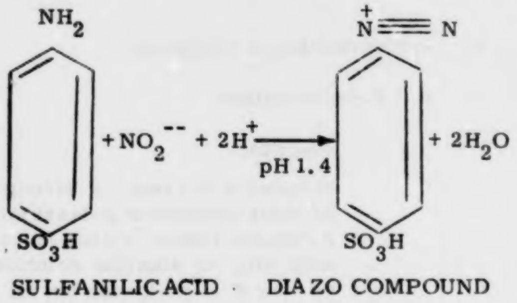
Table 1. ARS WATER NUTRIENTS, 1966

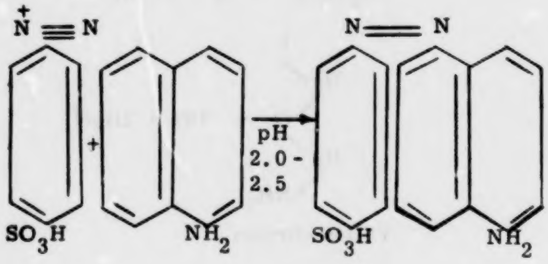
C Determination of Nitrite - Diazotization

1 Reaction

a Under acid conditions, nitrite ions react with sulfanilic acid to form a diazo compound.

b The diazo compound then couples with α-naphthylamine to form an intense red azo dye which exhibits maximum absorption at 520 nm.





2 Interferences

a Certain ions (e.g., Hg^{++}, Ag^+, Bi^{+++}, Sb^{+++}, Fe^{+++}, Pb^{++}) may interfere by precipitating during the test. A 0.5% EDTA solution may be used to complex iron.

b Cupric ion introduces negative interference by catalyzing decomposition of the diazo compound.

c Colored ions and turbidity may be removed by using $Al(OH)_3$ suspension or by flocculation with zinc sulfate and alkali.

3 Precision

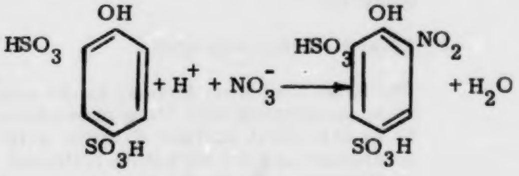
On a synthetic sample containing 0.25 mg nitrite nitrogen/l, the ARS Water Minerals Study (1961) reported 125 results with a standard deviation of ±0.029 mg/l.

D Determination of Nitrate

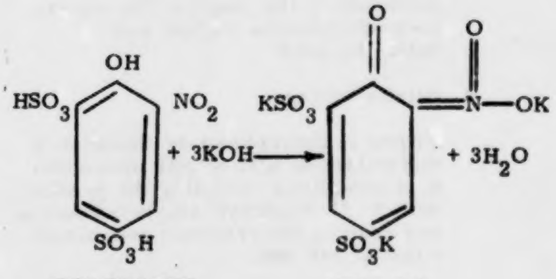
1 Phenoldisulfonic Acid

a Reaction

1) Phenoldisulfonic acid reacts with nitrate to produce a nitro derivative.



2) In alkaline solution the nitro derivative rearranges to form a yellow-colored compound which exhibits maximum absorption at 410 nm.;



b Interferences

1) Chlorine ion under the acid conditions of the test introduces negative interference.

$$6Cl^- + 2NO_3^- + 8H^+ \longrightarrow 3Cl_2 \uparrow + 2NO \uparrow + 4H_2O$$

Silver sulfate can be used to precipitate Cl^-, but due to incomplete precipitation of Ag^+, an offcolor or turbidity is produced when the final color is developed. (Note: This difficulty can be overcome by using NH_4OH as the alkali.)

2) Nitrites in concentrations greater than 0.2 mg N/l introduce positive interference. However, in most waters, the concentration of nitrite is insignificant compared to nitrate.

3) Color and turbidity may be removed by using $Al(OH)_3$ suspension or by flocculation with $ZnSO_4$ and alkali.

c Precision and accuracy

On a synthetic sample containing 1.0 mg nitrate N/l, and 200 mg Cl^-/l, the ARS Water Nutrients Study (1966) reported 46 results with a standard deviation of ±0.399 mg/l and a mean error of -0.31 mg/l.

2 Brucine

a Reaction

Brucine, a strychnine compound reacts with nitrate to form a yellow compound which exhibits maximum absorption at 410 nm. The reaction according to the procedure as outlined in Standard Methods does not follow Beer's Law. However, a recent modification by Jenkins and Medsker (2) has been developed. Conditions are controlled in the reaction so that Beer's Law is followed and concentrations below 1 mg nitrate N/l can be determined.

b Interferences

1) Nitrite may react the same as nitrate but can be elim-

inated by the addition of sulfanilic acid to the brucine reagent.

2) Organic nitrogen compounds may hydrolyze and give positive interference at low (less than 1mg/l) nitrate nitrogen concentrations.

3) Residual chlorine may be eliminated by the addition of sodium arsenite.

c Precision and Accuracy(8)

1) Twenty-seven analysts in 15 laboratories analyzed in natural water samples containing the following increments of inorganic nitrate: 0.16, 0.19, 1.08 and 1.24 mg N/liter.

2) Precision results as standard deviation were 0.092, 0.083, 0.245, and 0.214 mg N/liter respectively.

3) Accuracy expressed as bias was -0.01, +0.02, +0.04 and +0.04 mg N/liter, respectively.

3 Hydrazine Reduction

A method using hydrazine to reduce nitrate to nitrite followed by subsequent measurement of nitrite by diazotization was recently reported by Fishman, et al.(1) The procedure has been successfully adapted to the Auto Analyzer where a high degree of control of reaction conditions can be achieved.(3)

III EPA METHODS

A The Environmental Protection Agency, Office of Water Programs, Analytical Quality Control Laboratory, has compiled a manual of analytical methods for use by Federal laboratories. The title of this manual is "Methods for Chemical Analysis of Water & Wastes", 1971.

B The manual lists four nitrogen constituents. These are Ammonia Nitrogen, Total Kjeldahl Nitrogen, Nitrate Nitrogen and Nitrite Nitrogen.

1 Ammonia Nitrogen

The recommended procedures are either an automated method or distillation followed by titration (for high concentration samples) or Nesslerization (for low concentration samples).

2 Total Kjeldahl Nitrogen

The total Kjeldahl nitrogen is determined by an automated phenolate procedure, or by mercuric sulfate-sulfuric acid-potassium sulfate digestion followed by titration or colorimetric analysis

3 Nitrate Nitrogen

The automated method of determination involves reduction of the nitrate to nitrite with hydrazine, followed by colorimetric analysis The manual method is a spectrophotometric procedure in which a yellow color is produced by the reaction the nitrate ions with brucine sulfate and sulfanilic acid

4 Nitrite Nitrogen

Nitrite is determined by diazotizing sulfanilamide with nitrite ions under acid conditions, coupling the product with N- (1-Naphthyl) ethylenediamine, and reading the resultant red-purple color at 540 nm.

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7 ASTM Book of Standards, Part 23, 1970.

8 Methods for Chemical Analysis of Water & Wastes, EPA-AQCL, Cincinnati, Ohio 45268.

This outline was prepared by Betty Ann Punghorst, former Chemist, National Training Center and Charles Feldmann, Chemist, NTC, DTTB, MDS, WPO, EPA, Cincinnati, OH 45268.

SOURCES AND ANALYSIS OF ORGANIC NITROGEN

I INTRODUCTION

A Organic nitrogen refers to the nitrogen in combination with any organic radical. For sanitary engineering the main interest is the nitrogen contained in proteins, peptides, amines, amino acids, amides and related compounds of animal or vegetable origin.

II SOURCES OF ORGANIC NITROGEN

A Natural Origin

1 Dead animal and plant residues

2 Animal wastes - urea, feces

3 Autotrophic organisms - algae, s. bact.

4 Heterotrophic organisms

B Industrial Origin

1 Food processing wastewater - meat, milk, vegetables

2 Pharmaceutical wastes, antibiologicals

3 Plastics - polyamides, nitriles

4 Chemical intermediates or products

5 Dye industry - azo, nitro

III TOTAL KJELDAHL NITROGEN PROCEDURE

A Organic nitrogen is determined using the Total Kjeldahl Nitrogen (TKN) method. This determination includes both organic nitrogen and free ammonia. By distilling the free ammonia off the sample before the determination, organic nitrogen can be determined directly.

B Scope

The procedure converts nitrogen components of biological origin such as amino acids, proteins and peptides to ammonia but it may not convert the nitrogenous compounds of some industrial wastes such as amines, nitro compounds, hydrazones, oximes, semi-carbazones and some refractory tertiary amines.

C Method Summary(1)

The sample is heated in the presence of a concentrated sulfuric acid potassium sulfate-mercuric sulfate mixture and evaporated until sulfur trioxide fumes are obtained and the solution becomes colorless or pale yellow. The residue is cooled and diluted, then treated and made alkaline with a hydroxide-thiosulfate solution. The ammonia is distilled off and then determined either by nesslerization or by titration.

1 Nesslerization (colorimetric) is the method used when the ammonia-nitrogen concentration is less than 1.0 mg N/liter.

2 For ammonia-nitrogen concentrations above 1.0 mg N/liter, the ammonia is determined by titration with 0.02 N H_2SO_4 in the presence of a mixed indicator.

For a detailed description of the procedure and reagent preparation, consult the EPA methods manual.

D Precision and Accuracy

1 Thirty-one analysts in 20 laboratories(1) used the Total Kjeldahl Nitrogen procedure to analyze natural water samples containing the following increments of organic nitrogen: 0.20, 0.31, 4.10 and 4.61 mg N/liter.

a Precision results for a standard deviation were 0.197, 0.247, 1.056 and 1.191 mg N/liter, respectively.

b Accuracy as bias was +0.03, +0.02, +0.04 and -0.08 mg N/liter, respectively.

2 The nature and composition of extraneous materials affect analytical recovery. High salt concentrations may raise digestion temperature. High concentrations of organic sample components may require excessive acid during digestion tending to low nitrogen yield.

3 The digestion temperature is critical. 380 to 390°C usually gives high analytical recovery on the more refractory nitrogen compounds of natural origin. Nitrogen losses occur above 420°C.

E Optimum temperature is associated with a digestion mix containing 1 gram of potassium sulfate for each ml of sulfuric acid. However, the digestion mixture usually contains a fraction of H_2SO_4 greater than this.

During heating, the water boils off first, followed by fuming as the H_2SO_4 becomes concentrated. Fuming and oxidation of the sample components lead to loss of H_2SO_4 and a progressive decrease in acid content during heating. As the acid decreases, the temperature of the heated mixture rises.

Valid nitrogen determinations require a slight excess of acid to retain NH_3 as NH_4HSO_4 rather than the more volatile $(NH_4)_2SO_4$. Concurrently, excess acid will tend toward incomplete oxidation of sample components as a result of lowering digestion temperature.

IV AUTOMATED PHENOLATE METHOD

The EPA manual(1) also presents an automated (phenolate) method for organic nitrogen. The sample is automatically digested with a sulfuric acid solution containing potassium sulfate and mercuric sulfate as a catalyst, then neutralized with sodium hydroxide solution and treated with alkaline phenol reagent and sodium hypochlorite reagent. This treatment forms a blue color designated as indophenol. Sodium nitroprusside, which increases the intensity of the color, is added to obtain necessary sensitivity for measurement of low level nitrogen.

V PRESERVATION OF SAMPLES

A Most nitrogen compounds are characterized by rapid conversion from one form to another by biological and chemical action. Hydrolysis, deamination, peptide formation, and other reactions may appreciably alter the original form of sample nitrogen within a short time. Organic nitrogen tends to hydrolyze to free NH_3 during storage. Therefore, valid results require prompt analysis.

B Addition of 40 mg $HgCL_2$/liter of sample and storage at 4°C are preservation measures for samples. Even when so preserved, samples are unstable and should be analyzed as soon as possible.

REFERENCE

1 Methods for Chemical Analysis of Water and Wastes, EPA-AQCL. Cincinnati, OH 45268 (1971).

This outline was prepared by Audrey E. Donahue, Chemist, National Training Center, DTTB, MDS, WPO, EPA, Cincinnati, OH 45268.

DETERMINATION OF PHOSPHORUS IN THE AQUEOUS ENVIRONMENT

I Phosphorus is closely associated with water quality because of (a) its role in aquatic productivity such as algal blooms, (b) its sequestering action, which causes interference in coagulation, (c) the difficulty of removing phosphorus from water to some desirable low concentration, and (d) its characteristic of converting from one to another of many possible forms.

A Phosphorus is one of the primary nutrients such as hydrogen (H), carbon (C), nitrogen (N), sulfur (S) and phosphorus (P).

1 Phosphorus is unique among nutrients in that its oxidation does not contribute significant energy because it commonly exists in oxidized form.

2 Phosphorus is intimately involved in oxidative energy release from and synthesis of other nutrients into cell mass via:

a Transport of nutrients across membranes into cell protoplasm is likely to include phosphorylation.

b The release of energy for metabolic purposes is likely to include a triphosphate exchange mechanism.

B Most natural waters contain relatively low levels of P (0.01 to 0.05 mg/l) in the soluble state during periods of significant productivity.

1 Metabolic activity tends to convert soluble P into cell mass (organic P) as a part of the protoplasm, intermediate products, or sorbed material.

2 Degradation of cell mass and incidental P compounds results in a feedback of lysed P to the water at rates governed by the type of P and the environment. Aquatic metabolic kinetics show marked influences of this feedback.

3 The concentrations of P in hydrosoils, sludges, treatment plant samples and soils may range from 10^2 to 10^6 times that in stabilized surface water. Both concentration and interfering components affect applicability of analytical techniques.

II The primary source of phosphorus in the aqueous system is of geological origin. Indirect sources are the processed mineral products for use in agriculture, household, industry or other activities.

A Agricultural fertilizer run-off is related to chemicals applied, farming practice and soil exchange capacity.

B Wastewaters primarily of domestic origin contain major amounts of P from:

1 Human, animal and plant residues

2 Surfactants (cleaning agent) discharge

3 Microbial and other cell masses

C Wastewaters primarily of industrial origin contain P related to:

1 Corrosion control

2 Scale control additives

3 Surfactants or dispersants

4 Chemical processing of materials including P

5 Liquors from clean-up operations of dusts, fumes, stack gases, or other discharges

III Phosphorus terminology is commonly confused because of the interrelations among biological, chemical, engineering, physical, and analytical factors.

A Biologically, phosphorus may be available as a nutrient, synthesized into living mass, stored in living or dead cells, agglomerates, or mineral complexes, or converted to degraded materials.

B Chemically, P exists in several mineral and organic forms that may be converted from one to another under favorable conditions. Analytical estimates are based upon physical or chemical techniques necessary to convert various forms of P into ortho phosphates which alone can be quantitated in terms of the molybdenum blue colorimetric test.

C Engineering interest in phosphorus is related to the prediction, treatment, or control of aqueous systems to favor acceptable water quality objectives. Phosphorus removal is associated with solids removal.

D Solubility and temperature are major physical factors in phosphorus behavior. Soluble P is much more available than insoluble P for chemical or biological transformations and the rate of conversion from one to another is strongly influenced by temperature.

E Table 1 includes a classification of the four main types of chemical P and some of the relationships controlling solubility of each group. It is apparent that no clear-cut separation can be made on a solubility basis as molecular weight, substituent and other factors affect solubility.

F Table 2 includes a scheme of analytical differentiation of various forms of P based upon:

1 The technique required to convert an unknown variety of phosphorus into ortho P which is the only one quantitated by the colorimetric test.

2 Solubility characteristics of the sample P or more precisely the means required to clarify the sample.

a Any clarification method is subject to incomplete separation. Therefore, it is essential to specify the method used to interpret the yield factor of the separation technique. The degree of separation of solubles and insolubles will be significantly different for:

1 Membrane filter separation (0.5 micron pore size)

2 Centrifugation (at some specified rpm and time)

3 Paper filtration (specify paper identification)

4 Subsidence (specify time and conditions)

G Analytical separations (Table 2) like those in Table 1, do not give a precise separation of the various forms of P which may be included quantitatively with ortho or poly P. Conversely some of the poly and organic P will be included with ortho P if they have been partially hydrolyzed during storage or analysis. Insolubles may likewise be included as a result of poor separation and analytical conditions.

1 The separation methods provide an operational type of definition adequate in most situations if the "operation" is known. Table 2 indicates the nature of incidental P that may appear along with the type sought.

Table 1

PHOSPHORUS COMPOUNDS CLASSIFIED BY CHEMICAL AND SOLUBILITY RELATIONS

Form	Water Soluble(1)	Insoluble(1)
1. Ortho phosphates $(PO_4)^{-3}$	Combined with monovalent cations such as H, Na, K, NH_4	Combined with multi valent cations such as $Ca^{+2} Al^{+3} Fe^{+3}$
2. Poly phosphates $(P_2O_7)^{-4}, (P_3O_{10})^{-5} (P_3O_9)^{-3}$ and others depending upon the degree of dehydration.	as in 1 above Increasing dehydration decreases solubility	(a) as in 1 above (b) multi P polyphosphates (high mol. wt.) including the "glassy" phosphates
3. Organic phosphorus R-P, R-P-R (2) (unusually varied nature)	(a) certain chemicals (b) degradation products (c) enzyme P (d) phosphorylated nutrients	(a) certain chemicals (b) cell mass, may be colloidal or agglomerated (c) soluble P sorbed by insoluble residues
4. Mineral phosphorus	(a) as in 1 above	(a) as in 1 above (b) as in 2 above (c) geological P such as phosphosilicates (d) certain mineral complexes.

(1) Used in reference to predominance under common conditions.

(2) R represents an organic radical, P represents P, PO_4^{-3}, or its derivatives.

---

2 Total P in Table 2 includes liquid and separated residue P that may exist in the whole sample including silt, organic sludge, or hydrosoils. This recognizes that the feedback of soluble P from deposited or suspended material has a real effect upon the kinetics of the aqueous environment.

Table 2

PHOSPHORUS COMPOUNDS CLASSIFIED BY ANALYTICAL METHODOLOGY

Desired P Components	Technique(1)	Incidental P Included(2)
1. Ortho phosphates	No treatment on clear samples	Easily hydrolyzed (a) poly phosphates - (b) organic -P, - (c) Mineral -P, + or -
2. Polyphosphates (2)-(1) = poly P (hydrolyzable)	acid hydrolysis on clear samples, dilute (a) H_2SO_4 (b) HCl heated	(a) ortho-P + (b) organic -P + or - (c) mineral -P + or -
3. Organic phosphorus (3) - (2) + org P (hydrolyzable)	acid + oxidizing hydrolysis on whole sample. dilute (a) $H_2SO_4 + HNO_3$ (b) $H_2SO_4 + (NH_4)_2S_2O_8$ heated	(a) ortho P + (b) poly P + (c) mineral P + or -
4. Soluble phosphorus (preferably classified by clarification method)	clarified liquid following filtration, centrifugation or subsidence	generally includes (a) 1, 2, or 3 (b) particulates not completely separated
5. Insoluble phosphorus (residue from clarification)	Retained residues separated during clarification See (6)	(a) generally includes sorbed or complexed solubles.
6. Total phosphorus	Strong acid + oxidant digestion (a) $H_2SO_4 + HNO_3$ (b) $H_2SO_4 + HNO_3 + HClO_4$ (c) $H_2O_2 + Mg(NO_3)_2$ fusion	all components in 1, 2, 3, 4, 5 in the whole sample

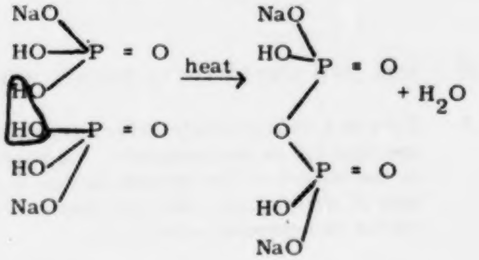
(1) Determinative step by phospho molybdate colorimetric method.

(2) Coding: + quantitative yield
- a small fraction of the amount present
+ or - depends upon the individual chemical and sample history

IV Polyphosphates are of major interest in cleaning agent formulation, as dispersants, and for corrosion control.

A They are prepared by dehydration of ortho phosphates to form products having two or more phosphate derivatives per molecule.

1 The simplest polyphosphate may be prepared as follows:



mono sodium ortho phosphate (2) disodium dihydrogen polyphosphate

2 The general form for producing polyphosphates from mono substituted orthophosphates is:

$$n\ (NaH_2PO_4)\ \xrightarrow[200\text{-}400^\circ C]{heat}\ (NaPO_3)_n + n\ H_2O$$

3 Di-substituted ortho phosphates or mixtures of substituted ortho phosphates lead to other polyphosphates:

$$2Na_2HPO_4 + NaH_2PO_4 \xrightarrow{heat} Na_5P_3O_{10} + 2H_2O$$

disodium hydrogen ortho phosphate + mono sodium di hydrogen ortho phosphate → pentasodium tri-phosphate + water

4 The polyphosphate series usually consist of the polyphosphate anion with a negative charge of 2 to 5. Hydrogen or metals commonly occupy these sites. The polyphosphate can be further dehydrated by heat as long as hydrogen remains. Di or trivalent cations generally produce a more insoluble polyphosphate than the same cation in the form of insoluble ortho phosphate. Insolubility increases with the number of P atoms in the polyphosphate. The "glassy" polyphosphates are a special group with limited solubility that are used to aid corrosion resistance in pipe distribution systems and similar uses.

B Polyphosphates tend to hydrolyze or "revert" to the ortho P form by addition of water. This occurs whenever polyphosphates are found in the aqueous environment.

1 The major factors affecting the rate of reversion of poly to orthophosphates include:

a) Temperature, increased T increases rate

b) pH, lower pH increases rate

c) Enzymes; hydrolase enzymes increase rate

d) Colloidal gels, increase rate

e) Complexing cations and ionic concentration increase rate

f) Concentration of the polyphosphate increases rate

2 Items a, b and c have a large effect upon reversion rate compared with other factors listed. The actual reversion rate is a combination of listed items and other conditions or characteristics.

3 The differences among ortho and ortho + polyphosphates commonly are close to experimental error of the colorimetric test in stabilized surface water samples. A significant difference generally indicates that the sample was obtained relatively close to a source of polyphosphates and was promptly analyzed. This implies that the reversion rate of polyphosphates is much higher than generally believed.

V SAMPLING AND PRESERVATION TECHNIQUES

A Sampling

1 Great care should be exercised to exclude any benthic deposits from water samples.

2 Glass containers should be acid rinsed before use.

3 Certain plastic containers may be used. Possible adsorption of low concentrations of phosphorus should be checked.

4 If a differentiation of phosphorus forms is to be made, filtration should be carried out immediately upon sample collection. A membrane filter of 0.45 μ pore size is recommended for reproducible separations.

B Preservation

1 If at all possible, samples should be analyzed on the day of collection. At best, preservation measures only retard possible changes in the sample.

   a Possible physical changes include solubilization, precipitation, absorption on or desorption from suspended matter.

   b Possible chemical changes include reversion of poly to ortho P and decomposition of organic or mineral P.

   c Possible biological changes include microbial decomposition of organic P and algal or bacterial growth forming organic P.

2 Refrigeration at 4°C is recommended if samples are to be stored. This decreases hydrolysis and reaction rates and also losses due to volatility.

3 Addition of 40 mg $HgCl_2$/liter is recommended for longer storage periods. This chemical limits biological changes.

   a $HgCl_2$ is an interference in the analytical procedure if the chloride level is low (See Part VI, B3).

VI THE EPA ANALYTICAL PROCEDURE(6)

A This is a colorimetric determination, specific for orthophosphate. Depending on the nature of the sample and on the type of data sought, the procedure involves two general operations:

1 Conversion of phosphorus forms to soluble orthophosphate (See Fig. 1):

   a sulfuric acid-hydrolysis for polyphosphates, and some organic P compounds.

   b persulfate digestion for organic P compounds.

2 The color determination involves reacting dilute solutions of phosphorus with ammonium molybdate and potassium antimonyl tartrate in an acid medium to form an antimony-phosphomolybdate complex. This complex is reduced to an intensely blue-colored complex by ascorbic acid. The color is proportional to the orthophosphate concentration.

Color absorbance is measured at 880 nm and a concentration value obtained using a standard curve.

Reagent preparation and the detailed procedure can be found in the EPA manual.

The methods described there are usable in the 0.01 to 0.5 mg/liter phosphorus range.

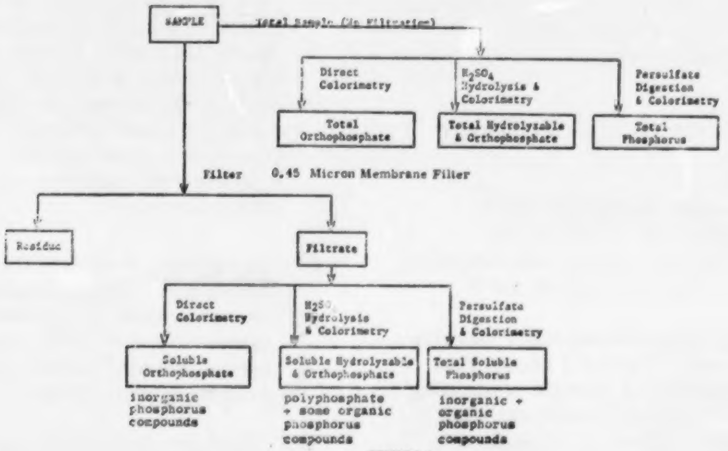

SAMPLE
Total Sample (No Filtration)
Direct Colorimetry
H_2SO_4 Hydrolysis & Colorimetry
Persulfate Digestion & Colorimetry
Total Orthophosphate
Total Hydrolyzable & Orthophosphate
Total Phosphorus
Filter
0.45 Micron Membrane Filter
Residue
Filtrate
Direct Colorimetry
H_2SO_4 Hydrolysis & Colorimetry
Persulfate Digestion & Colorimetry
Soluble Orthophosphate
Soluble Hydrolyzable & Orthophosphate
Total Soluble Phosphorus
inorganic phosphorus compounds
polyphosphate + some organic phosphorus compounds
inorganic + organic phosphorus compounds

FIGURE 1

ANALYTICAL SCHEME FOR DIFFERENTIATION OF PHOSPHORUS FORMS

B Interferences

1 Erroneous results from contaminated glassware is avoided by cleaning it with hot 1:1 HCl, treating it with procedure reagents and rinsings with distilled water. Preferably this glassware should be used only for the determination of phosphorus and protected from dust during storage. Commercial detergents should never be used.

2 High iron concentrations in samples can precipitate phosphorus.

3 If $HgCl_2$ is used as a preservative, it interferes if the chloride level of the sample is less than 50 mg Cl/liter. Spiking with NaCl is then recommended.

4 Others have reported interference from chlorine, chromium, sulfides, nitrite, tannins, lignin and other minerals and organics at high concentrations.

C Precision and Accuracy(6)

1 Organic phosphate - 33 analysts in 19 laboratories analyzed natural water samples containing exact increments of organic phosphate of 0.110, 0.132, 0.772, and 0.882 mg P/liter.

Standard deviations obtained were 0.033, 0.051, 0.130 and 0.128 respectively.

Accuracy results as bias, mg P/liter were: +0.003, +0.016, +0.023 and - 0.008, respectively.

2 Orthophosphate was determined by 26 analysts in 16 laboratories using samples containing orthophosphate in amounts of 0.029, 0.038, 0.335 and 0.383 mg P/liter.

Standard deviations obtained were 0.010, 0.008, 0.018 and 0.023 respectively.

Accuracy results as bias, mg P/liter were -0.001, -0.002, -0.009 and -0.007 respectively.

VII VARIABLES IN THE COLORIMETRIC PROCEDURE

Several important variables affect formation of the yellow heteropoly acid and its reduced form, molybdenum blue, in the colorimetric test for P.

A Acid Concentration during color development is critical. Figure 2 shows that color will appear in a sample containing no phosphate if the acid concentration is low. Interfering color is negligible when the normality with respect to H_2SO_4 approaches 0.4.

1. Acid normality during color development of 0.3 to slightly more than 0.4 is feasible for use. It is preferable to control acidity carefully and to seek a normality closer to the higher limits of the acceptable range.
2. It is essential to add the acid and molybdate as one solution.
3. The aliquot of sample must be neutralized prior to adding the color reagent.

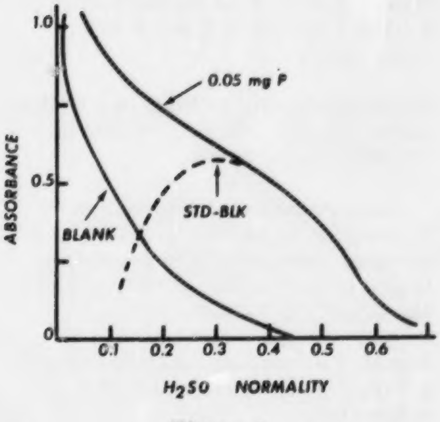


Figure 2

0-PHOSPHATE COLOR
VS ACIDITY

B Choice of Reductant - Reagent stability, effective reduction and freedom from deleterious side effects are the bases for reductant selection. Several reductants have been used effectively. Ascorbic acid reduction is highly effective in both marine and fresh water. It is the reductant specified in the EPA method.

C Temperature affects the rate of color formation. Blank, standards, and samples must be adjusted to the same temperature (± 1°C), (preferably room temperature), before addition of the acid molybdate reagent.

D Time for Color Development must be specified and consistent. After addition of reductant, the blue color develops rapidly for 10 minutes then fades gradually after 12 minutes.

VIII DETERMINATION OF TOTAL PHOSPHORUS

A Determination of total phosphorus content involves omission of any filtration procedure and using the acid-hydrolysis and persulfate treatments to convert all phosphorus forms to the test-sensitive orthophosphate form.

B Determining total phosphorus content yields the most meaningful data since the various forms of phosphorus may change from one form to another in a short period of time. (See part V, B1)

IX DEVELOPMENT OF A STANDARD PROCEDURE

Phosphorus analysis received intensive investigation; coordination and validation of methods is more difficult than changing technique.

A Part of the problem in methods arose because of changes in analytical objectives such as:

1 Methods suitable to gather "survey" information may not be adequate for "standards".

2 Methods acceptable for water are not necessarily effective in the presence of significant mineral and organic interference characteristic of hydrosoils, marine samples, organic sludges and benthic deposits.

3 Interest has been centered on "fresh" water, it was essential to extend them for marine waters.

4 Instrumentation and automation have required adaptation of methodology.

B Analysts have tended to work on their own special problems. If the method apparently served their situations, it was used. Each has a "favorite" scheme that may be quite effective but progress toward widespread application of "one" method has been slow. Consequently, many methods are available. Reagent acidity, Mo content, reductant and separation techniques are the major variables.

C At the present time there is not sufficient data to warrant EPA endorsement of the P procedure for sediment-type samples, sludges, algal blooms, etc. Following is a procedure (not included in the EPA manual) which is useful when solids are present in samples:

1 If sample contains large particles, grind and emulsify solids in a blender.

2 Transfer 50 ml sample, or aliquot diluted to 50 ml, into a 250 ml Erlenmeyer flask.

3 Add 6.0 ml of 18N H_2SO_4, 5 ml concentrated HNO_3, 2 berl saddles and digest on hot plate.

4 Digest until the disappearance of nitric acid fumes and the appearance of white SO_3 fumes. Continue digestion for approximately 5 minutes. Cool before proceeding with Step 5.

5 Add 2 ml of HNO_3-$HClO_4$ mixture and 5 ml concentrated HNO_3. Continue digestion until all of the nitric acid is driven off and dense fumes of perchloric evolve. Perchloric acid requires dilution with sulfuric acid and prior destruction of most organics for safety.

6 Cool. Add approximately 40 ml distilled water and transfer to 100 ml volumetric flask.

7 Add 2-3 drops of phenolphthalein and concentrated ammonium hydroxide until a pink color is seen. Then discharge the pink color with the strong sulfuric acid. It is advisable to add an equivalent amount of salt formed during neutralization of digested samples to the calibration standards to equalize salt content during color development.

8 Determine orthophosphate according to the usual color procedure.

ACKNOWLEDGMENT:

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This outline was prepared by Audrey E. Donahue, Chemist, National Training Center, DTTB, MDS, WPO, EPA, Cincinnati, OH 45268.

SOLIDS RELATIONS IN POLLUTED WATER

I MPN, oxygen demand, and solids have been major water pollution control criteria for many years. This discussion is concerned primarily with solids and their interrelations with oxygen demand.

A Engineered treatment or surface water self-purification depends upon:

1 The conversion of soluble or colloidal contaminants into agglomerated masses that may be separated from the water.

2 Oxidation of putrescible components into stable degradation products.

3 Item 1 is the major concern in most treatment systems because item 2 requires a greater investment in time, manpower and capital costs.

B Stress on oxygen demand removal frequently results in an unduly small amount of attention to the contribution of solids in the oxygen demand picture.

1 Oxygen demand formulations generally are specified to be applicable in the absence of significant deposition.

2 Increasing impoundment, tidal estuaries, and incomplete solids removal, generally ensure that solids deposition will be significant.

3 The BOD test stresses the fraction of oxygen demand that is exerted relatively rapidly. It includes only the fraction of unstable material that is exerted under test conditions - usually short term under aerobic conditions.

4 Contributions of a bed load of solids to oxygen demand frequently are incompletely recognized because they have a more local effect, are difficult to measure, tend to move, and are incompletely understood. The onset of an aerobic action in deposited solids increases hydrolysis rate. High molecular weight cell mass splits into small molecules that are soluble and more available for high rate oxidation upon feedback into oxygen containing water.

II A given wastewater may have several forms of solids in changeable proportions with time and conditions.

A Solids may be classified among the charted forms according to biological chemical or physical properties. It is not possible to precisely classify a given material into any one form because they usually are mixtures that may include or be converted into other forms.

B Interrelationships are indicated by diagram in Figure 1. Some changes occur more readily than others.

1 Settleable solids generally consist of a mixture of organic, inorganic, entrained dissolved or colloidal solids with living and dead organisms.

a They may be hydrolyzed into smaller sizes to aquire colloidal or dissolved characteristics.

b They may be converted into a larger fraction of living material or vice versa.

2 Colloidal solids also are likely to be a mixture of organic and inorganic materials, living or dead containing associated dissolved materials.

a They are likely to agglomerate to form settleable masses with time or changing conditions.

b Chemical reactions may solubilize the colloidal masses for recombination into other forms.

3 Dissolved solids are most readily available of all forms for biological, chemical or physical conversion.

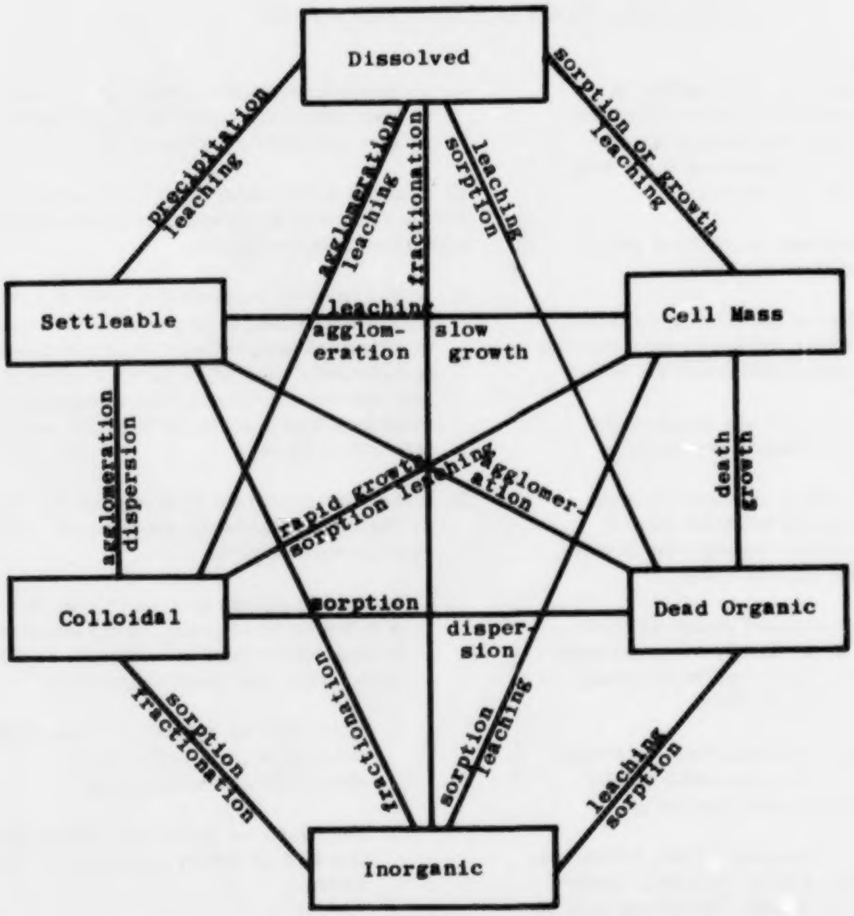
Dissolved
precipitation
leaching
agglomeration
leaching
fractionation
leaching
sorption
sorption or growth
leaching
Settleable
Cell Mass
leaching
agglomeration
slow growth
agglomeration
dispersion
rapid growth
sorption leaching
agglomeration
death
growth
Colloidal
Dead Organic
sorption
dispersion
sorption
fractionation
fractionation
sorption
leaching
leaching
sorption
Inorganic

Figure 1. SOLIDS INTERRELATIONSHIPS IN WATER

a They may be assimilated into cell mass to become colloidal during a state of rapid growth or form settleable masses during slow growth. Surface phenomena are likely to encourage inclusion of other forms of solids with cell mass.

C Stabilization occurs with each conversion because energy is expended with each change.

1 Biological changes involve oxidation to obtain enough energy to synthesize cells.

a Products consist of cell mass and degradation products.

b Oxidation tends toward production of CO_2, H_2O, NO_3^-, SO_4^{-2}etc. CO_2 has limited water solubility and partially leaves the aqueous environment. More soluble constituents tend to remain with it for recycle.

c Biological residues tend to recycle. Eventually the mass consists of relatively inert and largely insoluble residues. These make up the bed load that may decompose at a rate of less than 1% per day, but accumulates in mass until it becomes dominant in water pollution control activities.

III Treatment is an engineered operation designed to utilize events in surface water self-purification in a smaller package in terms of space and time. Effective treatment presupposes oxidation either in the plant or in facilities to minimize feedback of solids components to the aqueous environment.

A Primary treatment consists of a separation of floatable or settleable solids and removal from the used water.

1 Prompt removal is essential to minimize return of solubilized or leached materials from the sludge mass.

2 Sludge and scum are highly putrescible and difficult to drain.

3 Subsequent treatment prior to disposal serves to enhance drainability, reduce solids or volume for burial or burning.

B Secondary treatment generally involves some form of aerobic biological activity to oxidize part of the colloidal and dissolved contaminants and convert most of the remainder into a settleable sludge.

1 Aerobic systems favor assimilation of nutrients into cell mass at the expense of part of the available energy represented by oxidation to products such as CO_2 and water.

2 Cell mass and intermediate degradation products are only partially stabilized and tend to recycle with death and decay.

3 Rapid growth of cells tends to produce sludges that are highly hydrated and difficult to concentrate.

4 A compromise must be reached to produce a favorable balance among separation of solids and feedback of lysed materials.

a Cell growth continues as long as energy and nutrients permit.

b Under limiting nutrient conditions the population may show a relatively low rate overall dieoff but variety is changing.

c Species most favored by the new conditions tend to grow while others die, lyse and release part of their stored nutrients for subsequent use.

C Anaerobic digestion of solids separated during treatment is one process used to increase solids stability and drainability while reducing total volume or mass for disposal.

1 Growth of cell mass is relatively slow under anaerobic conditions while hydrolytic cleavage is relatively large in comparison to that during aerobic metabolism.

a Feedback to the aqueous environment represents a significant fraction of the input in the form of ammonia, colloidal solids, low molecular weight acids, and other products.

b Mass of the sludge is reduced by the fraction of methane, carbon dioxide, and other gases produced in process.

c Remaining solids tend to be more concentrated, are lower in putrescibility and give up their water more readily.

2 The liquid fraction of the products remaining after anaerobic digestion contain nutrients, oxygen demand, solids, and malodorous constituents that are objectionable in surface waters if released without further aerobic stabilization.

3 Digester liquids are much more concentrated than raw sewage and nutritionally unfavorable, hence they are difficult to treat and tend to shock aerobic treatment processes.

D Suitable disposal of solids resulting from treatment operations takes various forms of which the most desirable is to oxidize it completely to gaseous products of oxidation or inert ash. The objective is to limit feedback into the aqueous environment and delay the charted interchanges.

1 Deposition of sludge as a cover on crop land is effective providing surface drainage is properly designed to limit washoff.

2 Burial in areas above the flood plain provides a suitable disposal.

3 Incineration under controlled conditions to produce complete burning of organics is effective but requires close control.

a Incineration of digested sludge is feasible but the digestion process results in removal of part of the heat content of the sludge as methane carbon dioxide and water. Auxilary heat may be required for water evaporation if solids concentration is below 25%.

b Raw sludge incineration relieves the auxilary heat problem but storage may lead to odor problems. The raw sludge may require chemical treatment to enhance dewatering, secondary sludges are more difficult to dewater and may require centrifugation, floatation, or other treatment to concentrate sludge for heat balance purposes.

c Incineration requires close control of complex equipment to maintain acceptable environmental control. Usually, after burners and off gas scrubbers are necessary to avoid air pollution.

IV ANALYTICAL PROCEDURES

A The Analytical Quality Control Laboratory, Office of Water Programs, Environmental Protection Agency has published a manual titled, Methods for Chemical Analysis of Water and Wastes, 1971.

B In this manual solids are classified into four groups:

1 Total solids
2 Non-filterable (suspended) solids
3 Filterable (dissolved) solids
4 Volatile solids

C The procedure for the determination of 1, 2, and 3 above is given in the Analytical Quality Control Laboratory Manual.

Standard Methods for the Examination of Water and Wastewater, 13th Ed., page 538, Method 224D(1971) is the reference cited by the Analytical Quality Control Laboratory Manual.

This outline was prepared by F. J. Ludzack, Chemist, National Training Center, Water Program Operations, EPA, Cincinnati, OH 45268.

DETERMINATION OF SUSPENDED SOLIDS

I Wastewater stabilization includes the conversion of solid, liquid, or gaseous pollutants to (a) materials at a higher oxidation state or (b) to a more removable form. Both are interrelated, but (b) is favored during conventional treatment.

A Economics of treatment are more favorable when pollutants can be removed and treated in more concentrated form.

B Pollutant characteristics guide selection of operations applicable for contaminant conversion to suspended solids.

C Control of suspended solids removal is a major factor in treatment efficiency. Incomplete removal leads to feedback of nutrients from the unstable solids during later stages of stabilization.

II Characterization of the various forms of solids that may exist or be formed during stabilization of polluting materials necessarily depends upon operational factors. These are usually conditional, but their appreciation is essential.

A Dissolved solids include solid, liquid, or gaseous materials that are dispersed in the aqueous system in molecular or ionic form. The "solution" may be colored but it is likely to be clear unless the concentration of some items in the mixture approaches their solubility limits.

B Colloidal solids include a stage or condition of suspension where the solubility limit has been reached and the ionic or molecular dispersion tends to agglomerate to form "clumps" of insoluble materials or particulates. These particulates are large enough to scatter light and form cloudy or turbid suspensions but are not large enough to subside without further agglomeration.

C Suspended solids include the colloidally dispersed solids and the suspended solids that have agglomerated to form particulates that will subside or settle under quiescent conditions to form a solids concentrate or sludge. Size is a major criterion but density, shape, and interface characteristics among the liquid and solid are important factors.

D Total solids include A, B and C that may be present in the whole sample.

E Solids interrelationships are discussed in a prior outline. Determination of suspended solids is the object of this one.

III Sources of suspended solids include both Natural and man-made operations.

A Rainfall washes particulate material from the air and from the surfaces of forest, farmland, undeveloped land and urban or industrial centers.

B Municipal water supplies are controlled to maintain negligible suspended solids. Some may be formed in distribution systems.

C Groundwaters may contain dissolved solids that form suspended solids upon exposure to air or oxidation.

D Wastewaters are likely to contain varied suspended solids or components that may be converted to suspended solids by biological, chemical or physical transformations. Their nature varies with the origin such as household, commercial, industrial process, mining, washing, or other operations.

E Breaks below the groundwater level in partially filled sewers allow infiltration of suspended materials characteristic of the surrounding soils and water movement in them.

F Combined sewer systems, either intentional or otherwise, permit surface drainage from roofs, streets, parking lots, lawns, etc. to enter sanitary sewers.

IV The determination of suspended solids relate to operational factors determining the particular result obtained.

A A fence of wire or bars of appropriate sized openings may serve as a barrier to passage of horses and cattle but fail to stop cats or dogs.

B Smaller sized particles are commonly separated by filtration, centrifugation, subsidence, or other hydraulic gradation.

1 Roots, branches, rags, etc., usually are separated by bar racks or screens with relatively large openings.

2 Grit, sand and small, but heavy, particles generally are separated hydraulically in chambers allowing 1 to 3 minutes detention time.

3 Filtration is the most commonly applied technique for determination of the relatively low density particulates that tend to remain in aqueous suspension largely as a result of turbulence. Since pore sizes of filters differ, it is essential to specify the media used to interpret results.

V Standard Methods[1] refers to residues from whole sample evaporation as total residue, suspended solids as the non-filterable residue retained on or in the filter and dissolved residue as that appearing in the filtrate.

A Many factors influence the results obtained during suspended solids determinations such as

1 Chemical and physical nature of the solids

2 Sampling techniques

3 Pore size of the filter

A membrane filter of 0.5μ pore size may retain particulates that are not retained on paper.

4 Area, condition, and use of the filter affect particulate capture.

5 Technique and manipulative care in drying, weighing, storage, transfer, and temperature affect capture.

B Standard Methods includes three methods for non-filterable residue or suspended solids.

1 Gooch crucible

2 Membrane filter[2, 3]

3 Buechner funnel-aluminum dish (aerator or sludge suspended solids).

C A spectrophotometric method was described by Krawczyk and Gonglewski[4]. The importance of homogenization to improve sampling uniformity was stressed.

D Chanin, et. al.[5] described the use of glass fiber media for the determination of suspended solids.

VI Precision, sensitivity, and applicability of various methods for determination of suspended solids are indicated in the cited references.

A Table I indicates data from several references on precision of the Gooch crucible, asbestos fiber mat determination.

B Table 2 presents data published on the precision of the Gooch crucible, glass fiber determination.

C Smith and Greenberg[7] compared results of 5 replicates each of eight samples (influents, primary effluents, final effluents and industrial waste samples) by five different methods of determination including:

1 Gooch crucible, asbestos mat

2 Gooch crucible, glass fiber mat

3 Buechner funnel, wire cloth, glass fiber mat

TABLE 1

GOOCH CRUCIBLE ASBESTOS MAT

Range of Values mg/l	Ref.	Number of Replicates	Mean mg/l	Standard Deviation mg/l + or -	Sample Size Filtered ml
170-308	6	10	224	47	25
218-288	6	10	242	24	25
- -	7	5	360	13	50
- -	7	5	80	25	100
- -	7	5	104	8	100
- -	7	5	152	6	100
- -	7	5	1,023	79	25
- -	7	5	95	7	100
- -	7	5	297	27	50
- -	7	5	96	2	200
14-26	a	10	17	4	100
190-213	(d) 4	10	203	7	100
100-132	(d) 4	10	122	9	100
52-66	(d) 4	10	59	4	100

a Private communication, Lake Huron Program Office Methods Manual

TABLE 2

GOOCH CRUCIBLE FIBER FILTER

Range of Values mg/l	Ref.	Number of Replicates	Mean mg/l	Standard Deviation mg/l + or -	Sample Size Filtered ml
13-22	a	9	18	3	100
20-24	a	9	22	1	100
60-72	a	10	67	4	100
- -	6	5	1086	14	25
- -	6	5	361	47	50
- -	6	5	306	15	50
- -	6	5	146	3	100
- -	6	5	104	1	100
- -	6	5	100	1	100
- -	6	5	84	3	100
- -	6	5	79	5	100
104-436	5	12	296	119	25
60-196	5	14	111	38	25
8-152	5	11	100	54	25
56-100	5	9	76	17	50

4 Membrane filter 0.4 to 0.5 μ pore size

5 Gooch crucible, glass fiber mat, celite filter aid

a Their conclusions based upon carefully controlled technique indicated that yield and precision were not statistically different among the five tested methods.

b Determining factors other than in (a) included: manipulation time, required skills, speed of filtration, consistence of mat quality, equipment cost and availability.

c Methods 2 and 3 more frequently gave a lower coefficient of variation among those tested and were more favorable with respect to (b).

VII Section VI indicates that good results are possible among any of the tested methods but it was easier to obtain precise results with certain methods. The Gooch Crucible-asbestos mat requires a high degree of skill and manipulative time to provide consistent filtration. The membrane filter tends toward slow filtration, sampling or manipulative difficulties, and is more expensive.

A Certain precautions essential to consistent results with Gooch crucible-asbestos mats include:

1 A thin suspension of asbestos in distilled water is essential. A walnut-sized wad of fiber/1 is desirable.

2 Shake the suspension vigorously; allow it to settle 10-20 seconds. Pour the suspension into another container and discard asbestos slivers.

3 A more uniform suspension of asbestos is achieved after 10-30 seconds treatment in a Waring blendor or equivalent.

4 Allow to stand overnight or for a sufficient time to form an asbestos fiber concentrate on the bottom. Discard any milky fines in suspension and rewash, if necessary until a reasonably clear supernatant is obtained.

5 Insert the clean gooch crucible (30 ml or other selected size and diameter) into a Walters crucible adapter fitted to an 0.5 or 1 1 suction flask.

6 Shake the asbestos suspension vigorously, add the mixed suspension to the crucible until it is 1/2 to 2/3 full.

7 Allow the fiber to "mat" for 1/2 to 2 minutes, then apply vacuum slowly. If a hole forms in the mat the vacuum was applied too soon and too rapidly.

8 Add additional suspension (vacuum off) and apply vacuum to withdraw water and form a mat of 2-3 mm. Waiting period before vacuum application is not essential once a mat has formed. Water penetration rate is an effective means to judge mat quality. Good filtering is obtained if the exit stream from the Walters adapter is continuous but slow enough to be slightly off axis.

9 Wash the mat with successive portions of distilled water (200-250 ml) to clear the mat of fines.

10 Remove the crucible, wipe the outside with clean tissue or cloth and dry and weigh.

B Precautions and aids for glass fiber mat usage:

1 Gooch crucibles employing glass fiber mats of 2.4 cm diameter may encourage slow filtration; different shaped units such as the asphalt filtration crucible are designed to use larger diameter mats which may be desirable for aerator or sludge solids tests.

2 It is advisable to insert glass fiber mats with the smooth side up. A second mat may be required if the prewetting rinse

suggests unusually rapid water passage. Careful placement of the mat is essential.

C Membrane filter precautions include:

1 The filters are fragile and must be carefully handled to prevent damage during use.

2 Presoaking in distilled water for 24 hours helps to remove glycerol or other softening agent that is likely to be eluted by the sample.

3 Filters tend to curl on drying. An individual desiccator is described[3] that helps to control drying at ambient temperature and curling in process.

D Beuchner funnel suspended solids determinations include the (a) aluminum dish-paper, (b) wire cloth-glass fiber and (c) paper filtration. The aluminum dish is designed to support the paper and prevent losses during drying. The wire cloth promotes more rapid filtration and support. When neither supports are used, the paper or glass fiber may be folded once with the solids inside during drying.

1 Buechner funnel filtrations always present the problem of solids adherence to funnel sidewalls instead of the filter media. Solids losses due to incomplete transfer to the filter may be minimized but not eliminated. A square ended spatula aids transfer. It is advisable to adjust sample size to yield > 100 mg of non-filterable residue to reduce percentage error for Buechner funnel tests.

E General precautions applicable for precise results on suspended solids include:

1 Filters or crucibles must be clearly identified, dried, generally at 103°C, and stored in a desiccator until weighed and used.

2 The balance should contain a desiccant to control atmospheric moisture during weighing. This should be changed regularly and the doors opened only as necessary.

3 Filters may be dried in a desiccator (preferably 24 hours).

4 For rapid, control work with Buechner funnel-paper filtering, the papers may be oven dried and equilibrated with room moisture for 10 minutes to reduce changes due to rapid moisture pickup after oven drying.

5 Manufactured filters must be handled carefully with forceps, polished if necessary to prevent puncture or damage to the filter surface.

6 Place the filter media carefully in the crucible covering all openings in the support.

a Special care must be used for membrane filter holders to clamp the filter in place firmly without rupture or displacement.

7 Wet the filter media with distilled water preferably directed at the center of the mat first. Allow the mat to become thoroughly wet before applying vacuum then prewash the filter with about 100 ml of distilled water.

8 With the vacuum on, add the selected aliquot of sample.

a The sample volume should be large enough to minimize percentage errors during weighing. Less precise technique requires more weight difference between the pre and post filtration weights. Three to five mg weight difference is adequate for Gooch crucible technique, > 100 mg required for Buechner funnel tests. Homogenize the sample if sampling uniformity is questionable.

9 Rinse the non-filterable residue with distilled water to wash sidewall solids down onto the filter mat and to minimize occluded solubles in the solids and filter mat.

10 Dry and weigh under the same conditions as used for preweighing.

11 Final weight - Initial weight (mg)

$$\times \frac{1000}{\text{ml sample aliquot}} =$$

suspended solids in mg/l
Results are usually expressed in mg/l (g × 1000).

12 It is not feasible to dry suspended solids to a constant weight because of the interchange of moisture, volatiles or changes due to oxidation in process. Weight must be defined in terms of a routine that minimizes weight change errors.

13 It is not advisable to pre-ignite glass fiber mats for the determination of sample volatile solids as recommended for asbestos fiber mats. Glass fiber generally will soften at about 400° C but is likely to tolerate ignition at 550 to 600° C without fusion. It is advisable to check a given supply of fiber glass circles by igniting 5 or 6 under carefully controlled ignition temperatures and time sequence. If the glass fiber mats are uniform in weight and composition their weight loss on ignition will be comparable. This amount of ignition loss may be subtracted from the ignition loss for samples to obtain a corrected value for sample volatile suspended solids (VSS) if the loss is acceptably consistent.

14 The aluminum dish may be fabricated from an aluminum milk dish (listed in apparatus supply catalogues) by punching or drilling 1/16 inch holes in the bottom comparable to those of the Buechner funnel into which it is inserted. The aluminum dish and filter may be weighed before and after sample filtration and drying. An O ring of silicone M rubber slightly smaller than the dish may be used to provide a vacuum seal with the Buechner funnel. Sample contents must not overfill the dish during manipulation to avoid loss of solids by adherence to the funnel surfaces.

VIII The USEPA "Methods for Chemical Analysis of Water and Wastes", method for non-filterable solids (Storet number 00530) prescribes filtration through glass fiber media with drying at 105° C. (1971).

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PROCURING AND APPLYING LABORATORY BIO-OXIDATION DATA

I INTRODUCTION

A The purpose of process/development studies is the development of the design basis for a feasible and economical treatment process at a minimum of expense.

B The desired results can be realized by taking the following steps:

1 Characterize the wastes and the receiving system to determine what pollution characteristics must be minimized and the degree of treatment needed.

2 Develop fundamental treatability relationship in the laboratory.

C Pilot-scaled evaluation of design basis as determined in the laboratory is normally not justified because refinements in the design basis will be less significant than the engineering judgment which must be applied.

D The material in this outline is directed to the development of a design basis for the activated sludge process through laboratory-scaled procedures.

II DETERMINATION OF TOXICITY

A Determination of Toxicity Threshold to Seed Organisms

Make a series of dilutions of the waste in BOD bottles. A logarithmic series of 40, 20, 10, 5, 2, 1, 0.5, 0.2 and 0.1 percent by volume is suggested, but lower concentrations may be required for some wastes.

Add a constant quantity of an organic material to each dilution to serve as a control. Incubate the dilutions for three days. Idealized results obtained are illustrated in Figure 1. If the materials in the waste are not oxidized biologically and are not toxic or biostatic, the dissolved oxygen concentration after incubation will correspond to residual oxygen after depletion by the control. If there is no biological oxidation but toxicity exists, results similar to the solid line will be obtained. If there are organic materials present which are oxidized at lower concentrations of the waste with toxicity developing at higher concentrations of the waste, results similar to the dashed line will be obtained.

RESULTS FROM THE TOXICITY TEST
INDICATING A TOXIC CONDITION

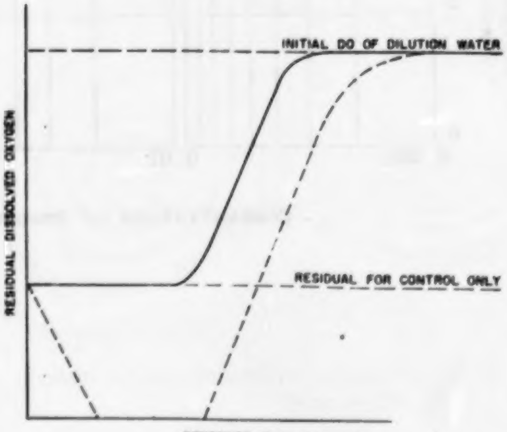


FIGURE I

In practical toxicity tests, oxygen consumptions due to biological oxidation should be distinguished from that due to chemical reactions. Toxicity data for an actual waste are shown in Figure 2. An organic control was not used. The circle points represent observations after incubation. The "x" points show oxygen consumption by chemical reaction determined as an immediate oxygen demand. The data show that toxicity existed and that consumption of oxygen at waste concentrations above 0.5 percent by volume were due to chemical reactions.

TOXICITY DATA FOR WASTE FROM INSECTICIDE MANUFACTURE

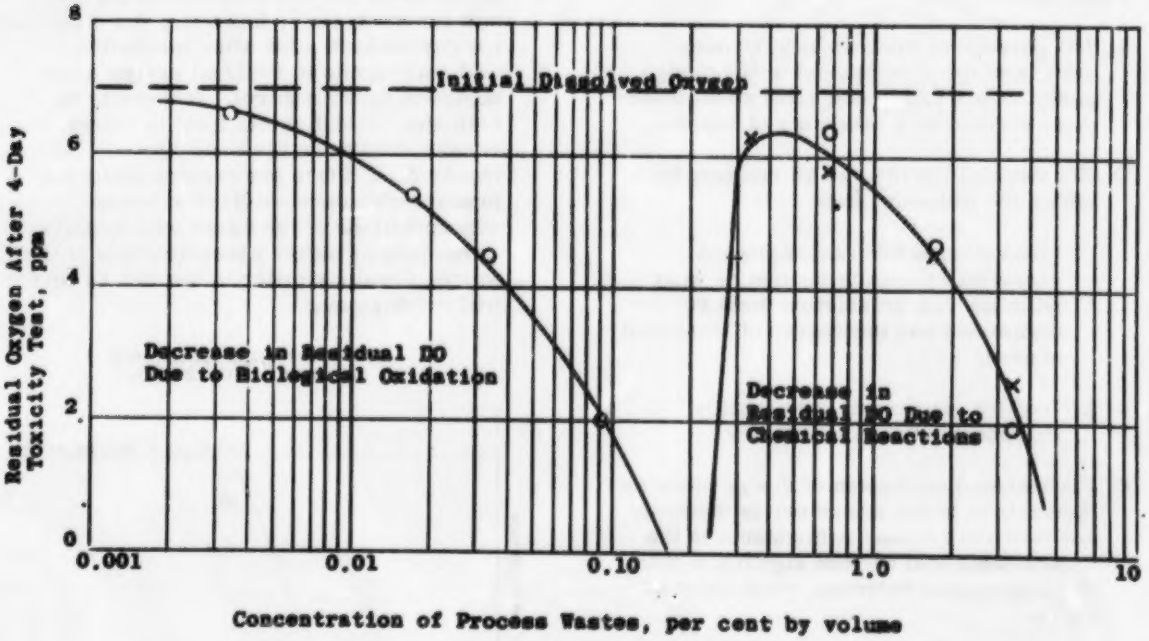


FIGURE 2

B Determination of Toxicity to Activated Sludge Systems

When an activated sludge culture exists and toxicity information is desired, direct respiration measurement can be made. A dissolved oxygen analyzer, a BOD bottle or equivalent, and a magnetic mixer are used to determine rate of oxygen consumption. The activated sludge culture should be in endogenous respiration, and this rate should be determined. The activated sludge is settled to obtain approximately double the concentration of biological solids in the mixed liquor. Waste equal in volume to the concentrated biological solids is added to the bottle. The system is oxygenated to some acceptable DO level (> 3 mg DO/liter) and then the rate of oxygen uptake is determined. The oxygen uptake rate should be significantly greater after feeding when compared to the endogenous rate.

The magnitude of increased uptake rate will be a function of the kind and concentration of organic material to be oxidized and the nature and concentrations of the biological culture. A range of concentrations of the waste may be examined to establish a toxicity threshold as indicated in a lower than expected oxygen uptake rate after the biological culture is fed.

III DEVELOPMENT OF FUNDAMENTAL DATA

A Basic Theory

1 ROY F. WESTON, INC. utilizes a fundamental relationship which defines the kinetics of a biological oxidation system in an overall sense. Two key features are involved - transfer of organic material and stabilization of organic material. The kinetic relationships can be observed most readily in the performance of a batch system. (1)

a BOD transfer kinetics

An idealized graphical model of BOD removal is presented in Figure 3. Following the feeding of a biological culture in a batch system, there is a decrease in the concentration of organic materials in the substrate due to biosorption and bioprecipitation reactions. Synthesis of the organic material into new cell material progresses at the same time. The decrease in substrate concentration continues until it is offset by releases of organic materials to the substrate due to endogenous reactions. At this point the number of microorganisms is in "equilibrium" with the available food supply.

Any biological system which is functioning dynamically must establish, as a mean, the "equilibrium" of microorganisms and food supply. Therefore, the balance of kinetics which represent the "equilibrium" condition are of primary interest. Based on the realization that the apparent kinetic of a batch system is reproducible, the development of kinetic constants was attempted in order to correlate the performance of batch and continuous activated sludge systems. The coefficient of BOD transfer was found to be

$$r = \frac{L_o - L_e}{L_e t_e}$$

GRAPHICAL MODEL OF BOD TRANSFER REACTION IN A BATCH SYSTEM

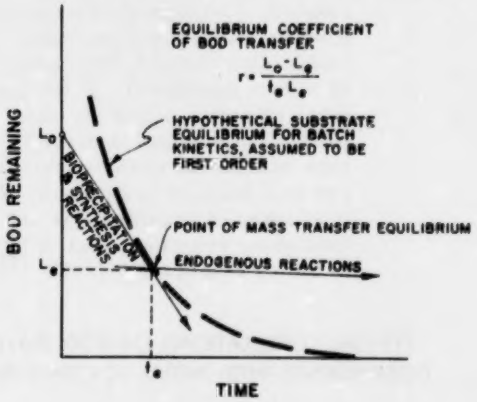


FIGURE 3

If the coefficient is assumed to be first order, and degree of completion of reaction (D) is taken as

$$D = 1-(1-r)^t$$

integration with mixing theory provides the process efficiency of a completely-mixed activated process,

(Ep) as

$$E_p = \frac{L_o - L_E}{} = \frac{r\,t_a}{1 + r\,t_a}$$

r = reaction rate in terms of oxygen where L_o is the influent to the process, L_E is the effluent and t_a is the aeration period. If the value of r is calculated from the process variables,

$$r = \frac{L_o - L_E}{L_E t_a}$$

Therefore, values of "r" can be calculated from either batch or continuous data and will agree in value.

The BOD transfer coefficient correlates with the food-to-microorganisms ratio, L_o/S_o. Correlations generally encountered are illustrated in Figure 4. The reaction rate coefficient as calculated, correspond to a specific food-to-microorganism ratio (suspended solids taken as mass of microorganisms). If the true mass of active organism were known (instead of suspended solids) the rate coefficient could be calculated per unit mass of organisms. Since true mass of organisms is not available, reaction mass is ignored in the calculation (MLVSS). (2)

TYPICAL CORRELATIONS OF BOD TRANSFER COEFFICIENTS WITH INITIAL LOADING RATIOS

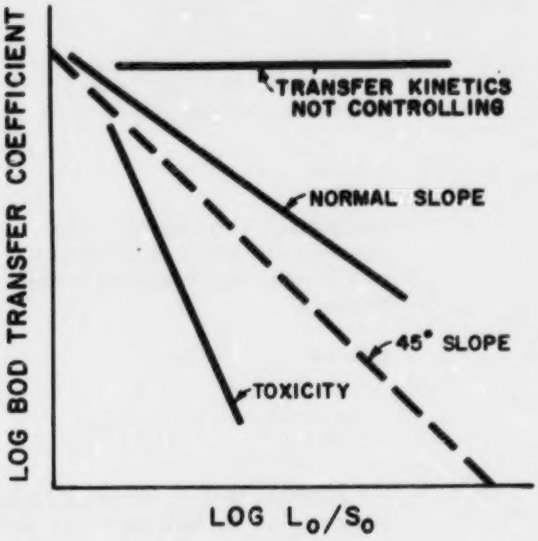


FIGURE 4

The 45° slope in Figure 4 represents the theoretical change in transfer coefficient that is anticipated as L_o/S_o is varied. If the concentration of biological mass is doubled (which reduces the L_o/S_o ratio by one-half) the BOD transfer coefficient is expected to double. In the activated sludge systems examined, the slope of the correlation is somewhat less than 45° as indicated by the line of "normal slope". In some activated sludge systems, the performance of the system is not controlled by transfer kinetics, and this condition will be indicated by a BOD transfer coefficient which is independent of the food-to-microorganism ratio. If toxicity exists in the wastewater, the correlation will have a slope greater than 45° because increased concentration of food material (and the associated toxicity) suppresses biological activity.

b Stabilization kinetics

BOD transfer kinetics define one aspect of an activated sludge system. The overall sequence of events must involve transfer followed by conversion of the organic material into new cell material and/or stable end products. The reactions involved after transfer are referred to as stabilization. Stabilization can be observed through consumption of oxygen by the biological system. The oxygen is utilized in the energy transport system which supports synthesis reactions.

In Figure 5 two cases which may occur in activated sludge systems are illustrated. In one case, the organic material is stabilized as rapidly as it is removed. This condition is indicated by the decrease in rate of oxygen utilization at essentially the same time that transfer "equilibrium" is reached. In the other case, stabilization proceeds for a significant period of time after transfer "equilibrium" has been reached and indicates that the rate of stabilization is slower than the rate of transfer.

TYPICAL RELATIONSHIPS BETWEEN BATCH KINETICS OF BOD TRANSFER AND STABILIZATION REACTIONS

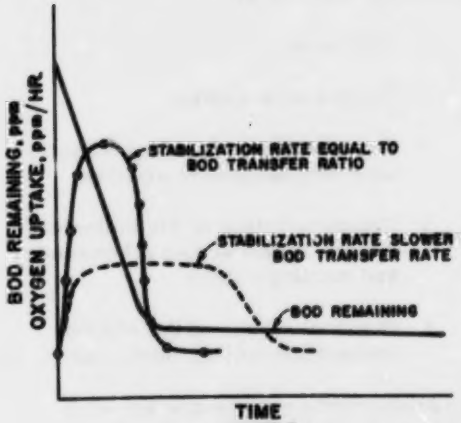


FIGURE 5

By utilizing the time required for stabilization to be completed, t_s, and the BOD remaining at that time, L_S, a stabilization rate coefficient can be calculated as

$$r_s = \frac{L_o - L_S}{L_S t_s}$$

As far as overall kinetics in the activated sludge process are concerned, the stabilization kinetics control. If a single aeration basin is utilized, aeration periods must accommodate the stabilization kinetics. Knowledge of transfer and stabilization kinetics are the basis for design of modifications of the activated sludge process such as contact-stabilization.

B Acclimation of Microorganisms in a Continuous System and the Collection Data

1 Apparatus

Figure 6 shows a suitable apparatus for use as a bench-scaled activated sludge system. A portion of the volume of the container is blocked off to serve as a clarification section. However, in current practice an aeration container and an external clarifier are used in order to provide increased flexibility of operation.(3) The aeration container ranges from a plastic wastepaper basket to a 55-gallon drum depending upon the volume desired, and the clarifier is a glass cone called a percolator or a plexiglas cylinder with a conical bottom. The clarifier is generally equipped with a slow speed stirrer and scraper to move sludge. The feed of wastewater and the returned sludge are pumped.

The selected size of the aeration system depends upon the wastewater strength and the desired detention time. Slow pumping rates are difficult; therefore, for longer detention times, larger aeration volumes are desirable. Also, lower organic loadings of high strength wastes require a larger aeration volume to permit a faster pumping rate.

2 Two approaches may be applied for the acclimation and growth of a culture of microorganisms.

a An available activated sludge culture may be utilized as the source of microorganisms with the normal feed to that system being gradually replaced by the wastewater under investigation until performance of the wastewater is obtained.

APPARATUS FOR A CONTINUOUS BIOLOGICAL OXIDATION SYSTEM

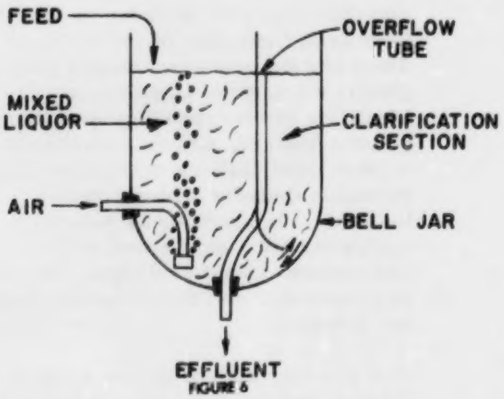


FIGURE 6

b Culture development can begin with a small quantity of seed organisms and a feed of wastewater diluted below the toxicity threshold (if toxicity exists). As the biological mass develops, the toxicity threshold is re-determined and wastewater concentration is increased accordingly until the culture is capable of handling wastewater at 100 percent concentration.

Technique b is preferred because it provides the best opportunity to observe the growth characteristics of the biological culture as well as potential problems with acute or chronic toxicity.

3 When the culture is capable of functioning on the undiluted wastewater, data are collected on the performance of the system beginning with a low feed rate (approximately 20 mg BOD_U/hr) and increasing the feed rate until performance near that for the anticipated design is achieved. At the conditions of various organic loadings, the performance and characteristics of the system are evaluated in terms of:

a BOD removal (preferably ultimate carbonaceous)

b COD removal

c Oxygen consumption

d Concentration of biological solids (and dehydrogenase activity)

e Characteristics of the biological culture (microscopic appearance and settling rates)

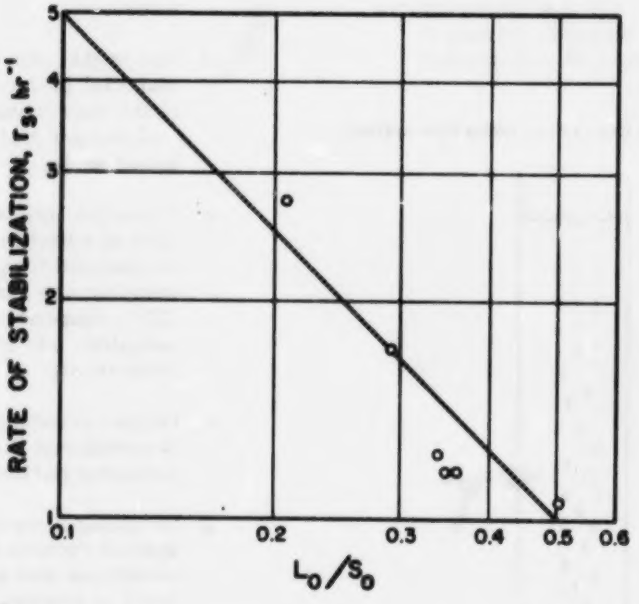
f Physical nature of the effluent (suspended solids, odor, color, etc.)

Characteristic results are shown in Figure 7 which were developed in an apparatus similar to that shown in Figure 6.

In Figure 8 the coefficient of stabilization has been calculated from the continuous data and correlated to the food-to-microorganism ratio.

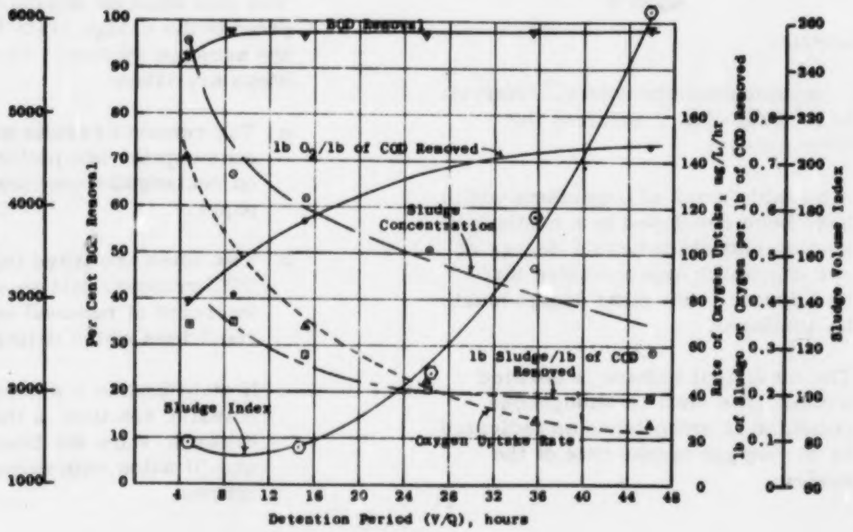
C Batch Technique for the Development of Kinetics

Batch procedures provide the opportunity to separate kinetics in the activated sludge process into the two functions of organic material transfer and stabilization. The information is valuable because it permits the development of design bases for modifications of the activated sludge process which have improved process stability, but the procedure is practical only if toxicity is insignificant.



STABILIZATION KINETICS CALCULATED FROM CONTINUOUS DATA FROM FIGURE 14

FIGURE 7



ACTIVATED SLUDGE TREATMENT OF A SYNTHETIC WASTE (DEXTROSE, 1500 mg/L)
DATA DETERMINED IN A CONTINUOUSLY-FED OXYGEN UTILOMETER

FIGURE 8

1 Apparatus

Any container of suitable volume (normally 8 to 12 liters) fitted with an aerator can be utilized. Figure 9 illustrates a tube with aerator and sampling valve.

APPARATUS FOR BATCH BIOLOGICAL OXIDATION SYSTEMS

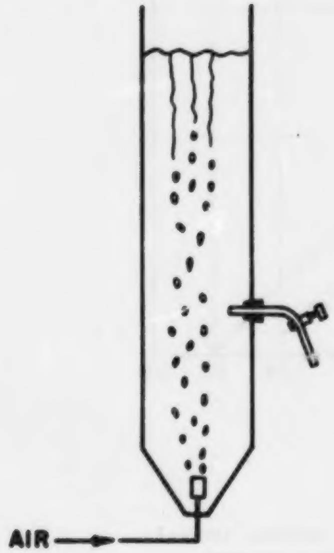


FIGURE 9

2 Procedure

The experimental procedure, referred to as a "Tube-Run", involves the following steps:

- a A suitable mass of organisms which have been developed in a continuous system and which have a degree of activity which approximates that anticipated in the final design must be available.
- b The biological culture is aerated without feed until an endogenous condition is established as indicated by the oxygen uptake rate of the system.
- c A logarithmic series of food-to-microorganisms is prepared in separate containers (usually four tubes).
- d The initial concentration of organic material is determined on the basis of the supernatant from the biological culture and the wastewater feed added to the particular tube.
- e From the time that the wastewater feed is added to culture, the system is sampled frequently, and the samples are analyzed for BOD, COD, suspended solids on some samples, and any other analyses of interest.
- f Oxygen consumption by the system is monitored throughout the sampling period.
- g Sampling is continued until the system returns to endogenous conditions and until the "equilibrium" level of organic material under endogenous conditions is established.

3 Interpretation of Data for Organic Material Removal

The data must be interpreted to provide the design basis for size of the aeration system. The following steps are taken:

- a The removal results and oxygen consumption are plotted vs time on rectangular coordinate graph paper.
- b Two lines are fitted through the BOD removal data to show the intercept of removal and endogneous conditions which defines L_e and t_e.
- c If stabilization kinetics differ from transfer kinetics, a third line is drawn to show the intercept of stabilization with endogenous conditions.

d **The coefficients of transfer and stabilization are calculated.**

e The coefficients are correlated with food-to-microorganism ratios.

f From the performance of the continuous system and from process considerations, a practical value of L_o/S_o is selected.

g Based on the value of coefficients which correlate with the L_o/S_o value, the detention time which provides the desired process efficiency are calculated from the equation in Section III, A, a. The value of detention time, ta, is

$$Ep = \frac{rt_a}{1 + rt_a} \qquad t_a = \frac{E_p}{r\,(1 - E_p)}$$

4 Interpretation of data for oxygen requirements

Oxygen utilization in the batch system is composed of energy oxygen and endogenous oxygen as illustrated in Figure 10. Energy oxygen is calculated from each tube of the "Tube Run" by selecting the area attributable to endogenous respiration and planimetering the remaining area to determine mg/l of oxygen. The oxygen consumed is correlated with removal of BOD or COD. The weight of oxygen required per weight of BOD or COD removed is essentially a constant (exceptions do exist).

The endogenous level shown in each tube of the "Tube Run" reflects the recent product of a population of new cells and as a result is higher than a practical value. A practical value can be obtained from the continuous data if the system is taken to endogenous condition periodically during the operating period. Endogenous respiration is conveniently expressed as weight of oxygen required per unit of time per weight of activated sludge under aeration.

CONSUMPTION OF OXYGEN BY A BATCH BIOLOGICAL OXIDATION SYSTEM

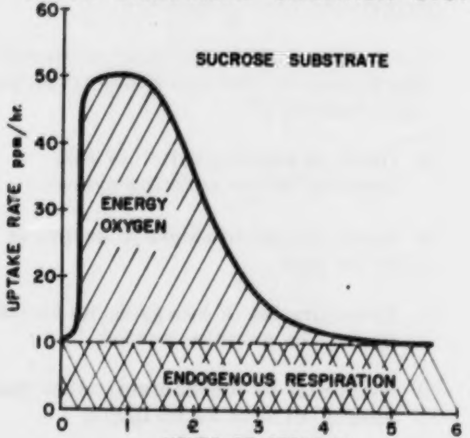


FIGURE 10

Total oxygen requirement, pounds per hour, can be calculated as

Energy Oxygen, lbs/lb of BOD removed — Maximum Rate of BOD Removal, lbs/hr +

Endogenous respiration, lbs/hr/1000 lbs of sludge under aeration — Number of thousands of pounds of sludge under aeration

5 Estimation of sludge production

If the assumption is made that organic material removed from the system either enters into energy reactions or is synthesized into new cell material, total synthesis S_s, can be estimated as

$$S_s = \frac{1 - O_E}{1.42}$$

The value 1.42 is approximately equivalent to the pounds of COD per pound of cell material, and O_E is the fractional weight ratio of energy oxygen and COD removed.

Conversion of the estimated synthesis into a practical net synthesis requires consideration of

a Rates of auto-oxidation of cell material in the aeration system

b Inputs of non-biodegradable solids in the feed

c Precipitation of inorganic materials during the aeration period

d Removals by mechanisms other than biological such as stripping

e Losses of solids in the effluent

6 Estimation of the effect of temperature

The reaction rate coefficient varies with temperature. An estimate of the variation in r can be obtained from the relationship.

$$\log (1 - r)\, t_2 = \log (1 - r)\, t_1 \cdot 1.042^{(t_2 - t_1)}$$

7 Examples of actual data

Three actual sets of Tube Run data are presented which were selected for illustration of significant and interesting results.

Case No. 1

The wastewater are from refinery and chemical manufacturing operations. As the results from the four tubes (Figures 11, 12, 13, 14) are scanned, the following observations are made:

a The BOD removal is relatively rapid.

b Oxygen uptake rate rises quickly immediately after the batch system is initiated.

c Oxygen uptake rate returns to the endogenous level at approximately the same time that BOD concentrations reach endogenous condition.

d The calculations are not shown, but energy oxygen in each tube is essentially constant even though initial mixed liquor volatile solids range from 424 to 3454 mg/l.

The coefficients of transfer and stabilization are the same because BOD removal and oxygen consumption follow the same pattern. The correlation of the transfer coefficient and the food-to-microorganisms ratio is shown in Figure 15.

Case No. 2

The wastewaters are from the manufacture of textile dyestuff. Development of BOD data was peculiar because the BOD curves for raw wastewater lagged extensively even when acclimated microorganisms from the bench-scaled activated sludge system were used as seed. After biological treatment, the BOD curve had no lag. Thus, on the basis of 5-day BOD values biological treatment always produced BOD.

A scan of the four tubes of the "Tube Run" (Figures 16, 17, 18, 19) show that:

a The oxygen uptake develops gradually from the initiation of the system and ends abruptly when BOD removal is complete.

b The energy oxygen requirement is essentially constant across the range of mixed liquor volatile solids.

c Rate of removal of organic material is relatively slow.

FIGURE 11

CASE No.1

REFINING AND CHEMICAL WASTEWATERS

LABORATORY ACTIVATED SLUDGE DATA

TUBE I

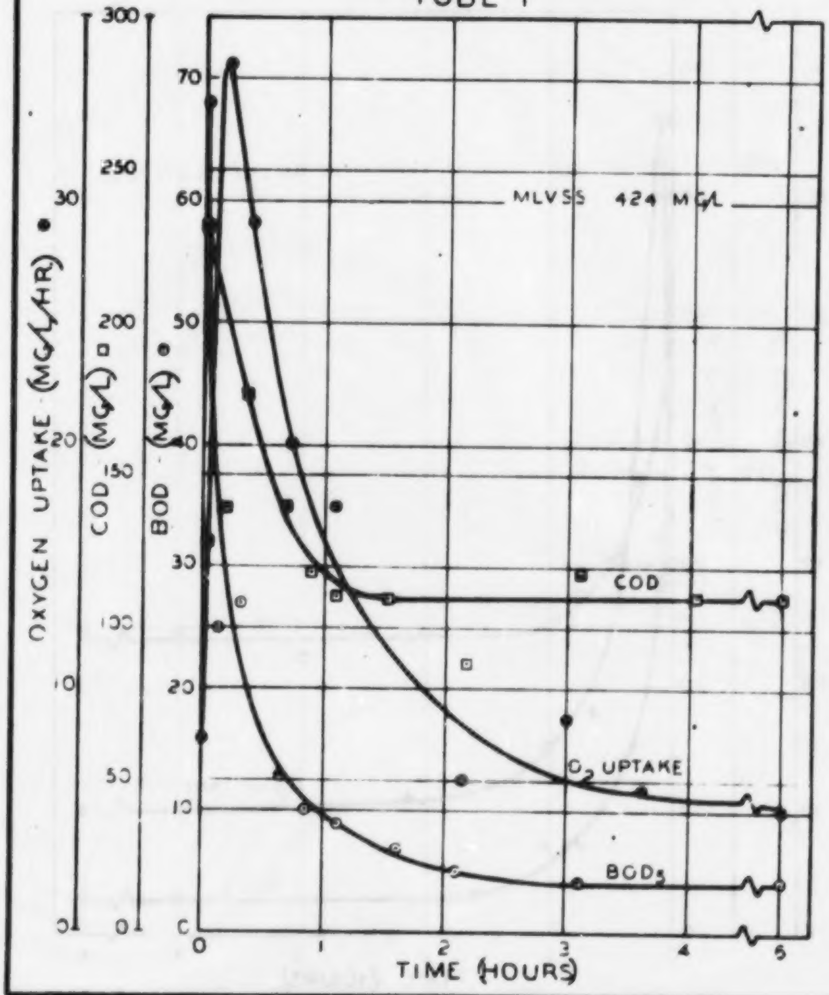


FIGURE 12
CASE No.1
REFINING AND CHEMICAL WASTEWATERS
LABORATORY ACTIVATED SLUDGE DATA
TUBE 2

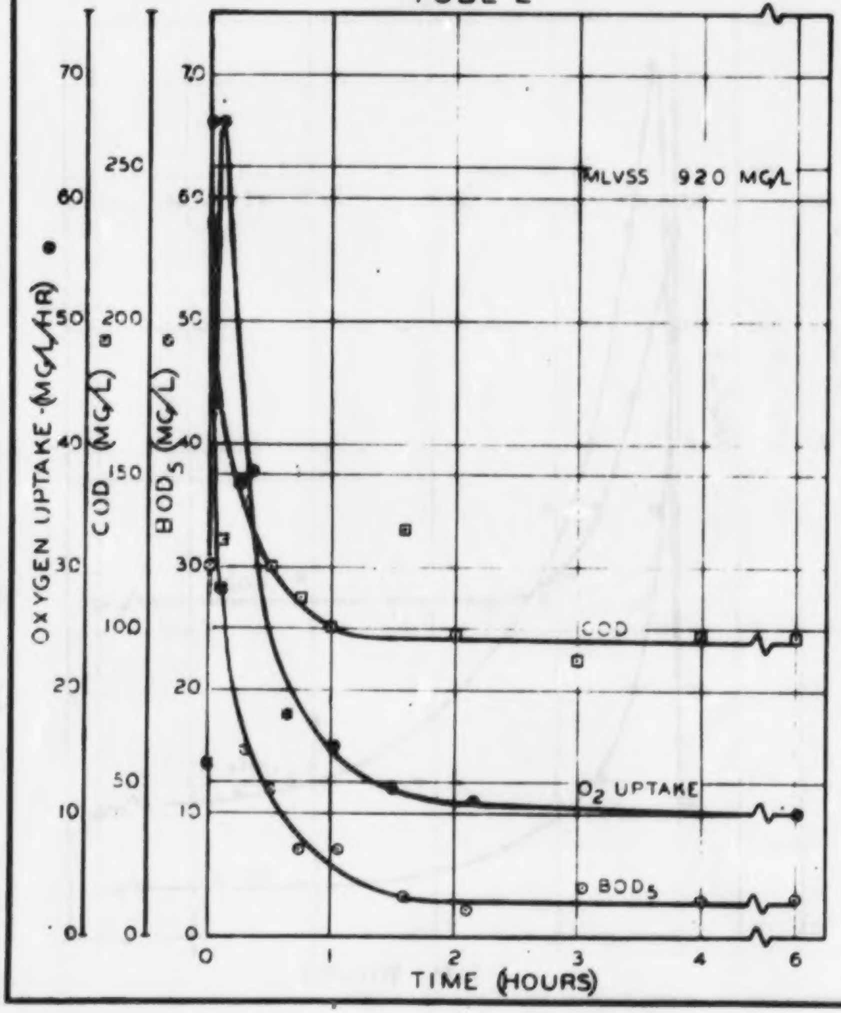


FIGURE 13
CASE No.1
REFINING AND CHEMICAL WASTEWATERS
LABORATORY ACTIVATED SLUDGE DATA
TUBE 3

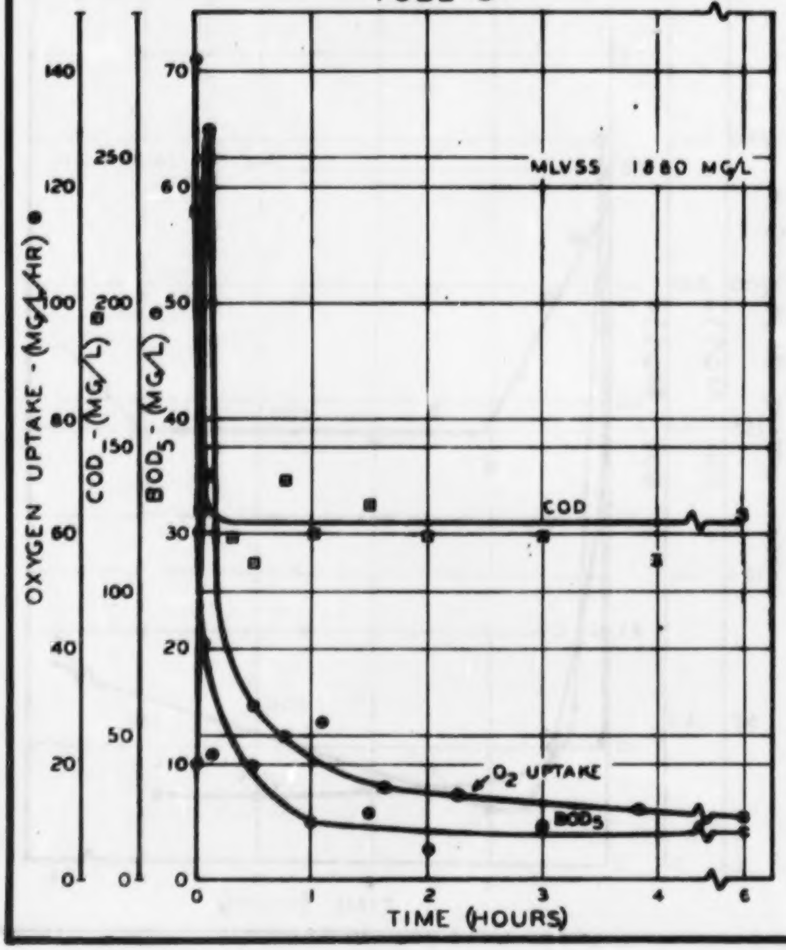


FIGURE 14
CASE No.1
REFINING AND CHEMICAL WASTEWATERS
LABORATORY ACTIVATED SLUDGE DATA
TUBE 4

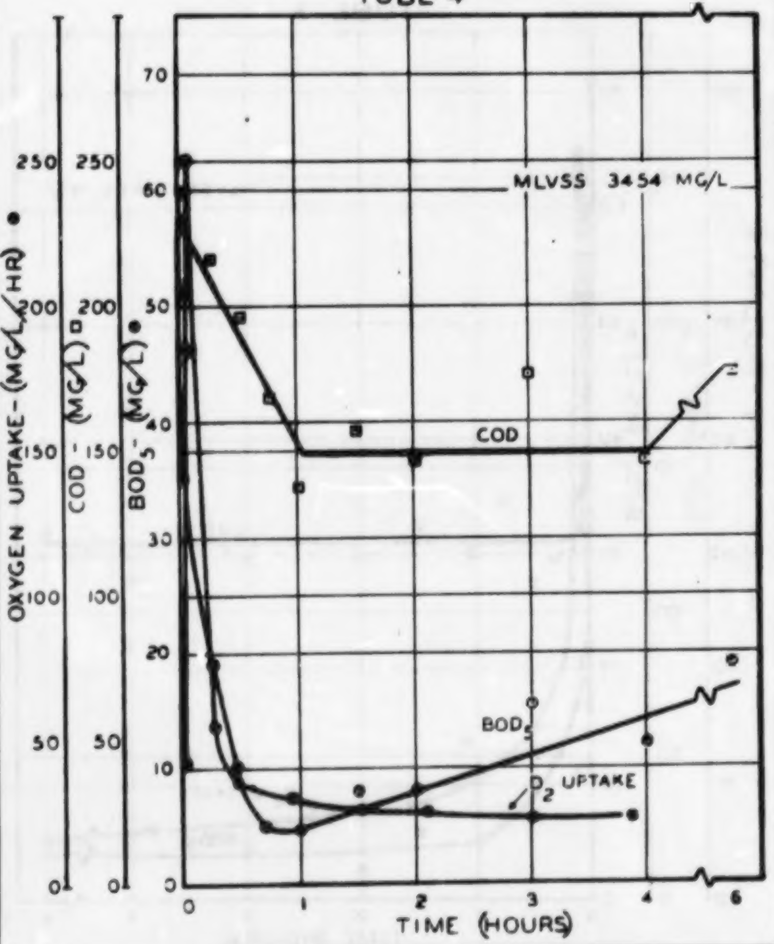


FIGURE 15
CASE No.1
REFINING AND CHEMICAL WASTEWATERS

BOD_5 REMOVAL COEFFICIENT
VS
BOD_5 LOADING RATIO

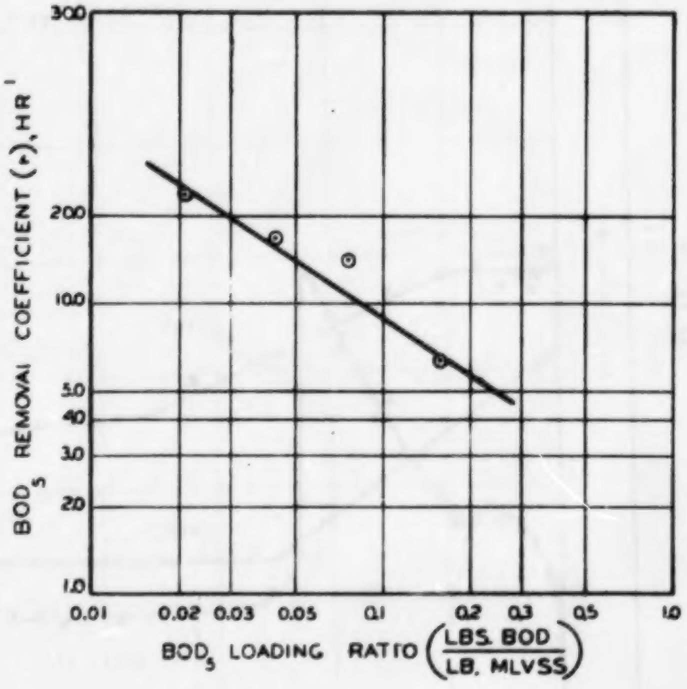


FIGURE 16
CASE No.2
TEXTILE DYESTUFFS WASTEWATERS
LABORATORY ACTIVATED SLUDGE DATA
TUBE NO. 1

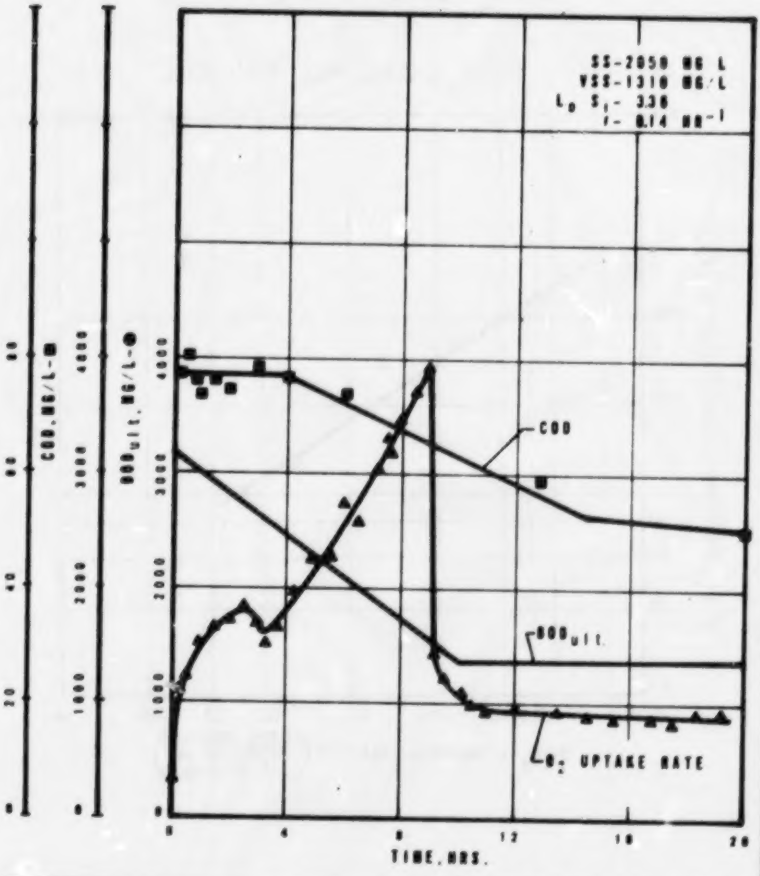


FIGURE 17
CASE No.2
TEXTILE DYESTUFFS WASTEWATERS
LABORATORY ACTIVATED SLUDGE DATA
TUBE NO. 2

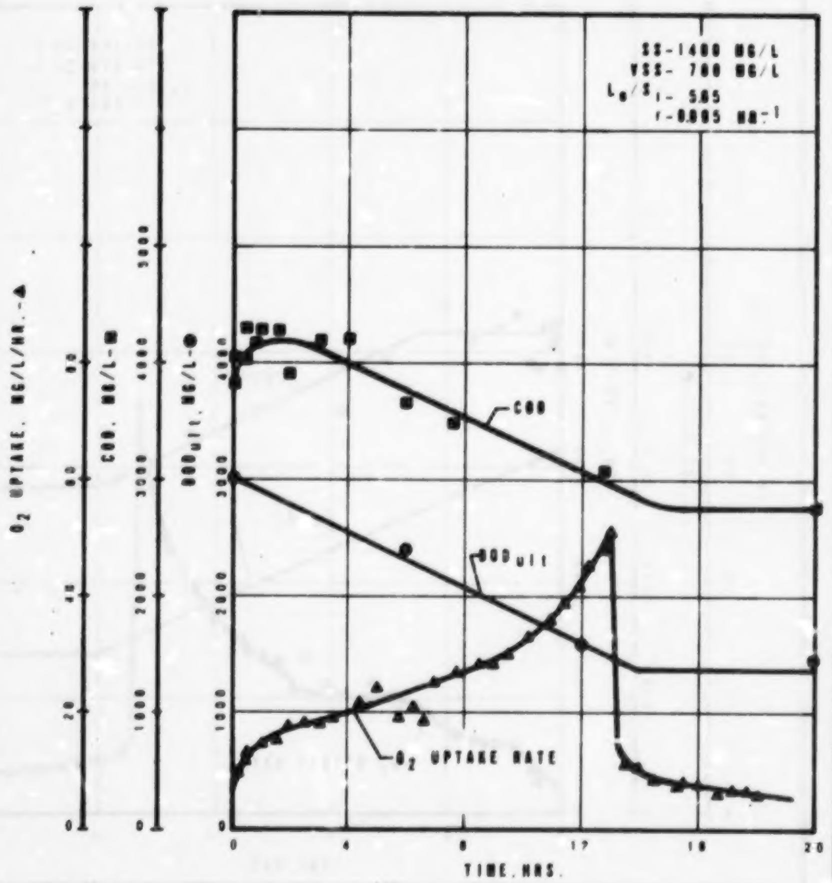


FIGURE 18
CASE No.2
TEXTILE DYESTUFFS WASTEWATERS
LABORATORY ACTIVATED SLUDGE DATA
TUBE NO. 3

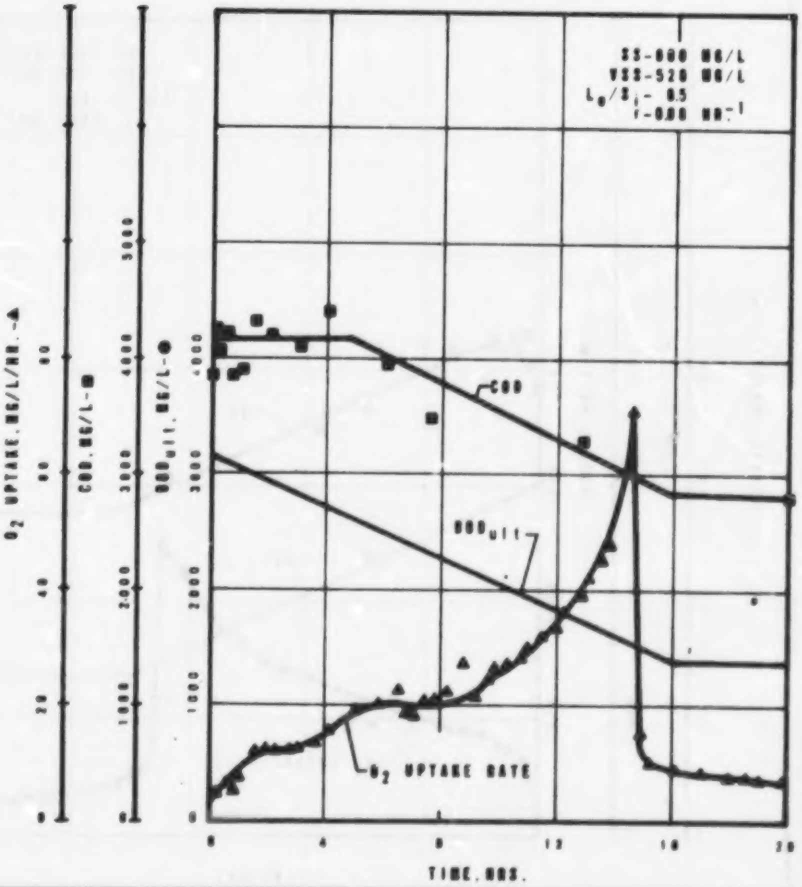


FIGURE 19
CASE No.2
TEXTILE DYESTUFFS WASTEWATERS
LABORATORY ACTIVATED SLUDGE DATA
TUBE NO. 4

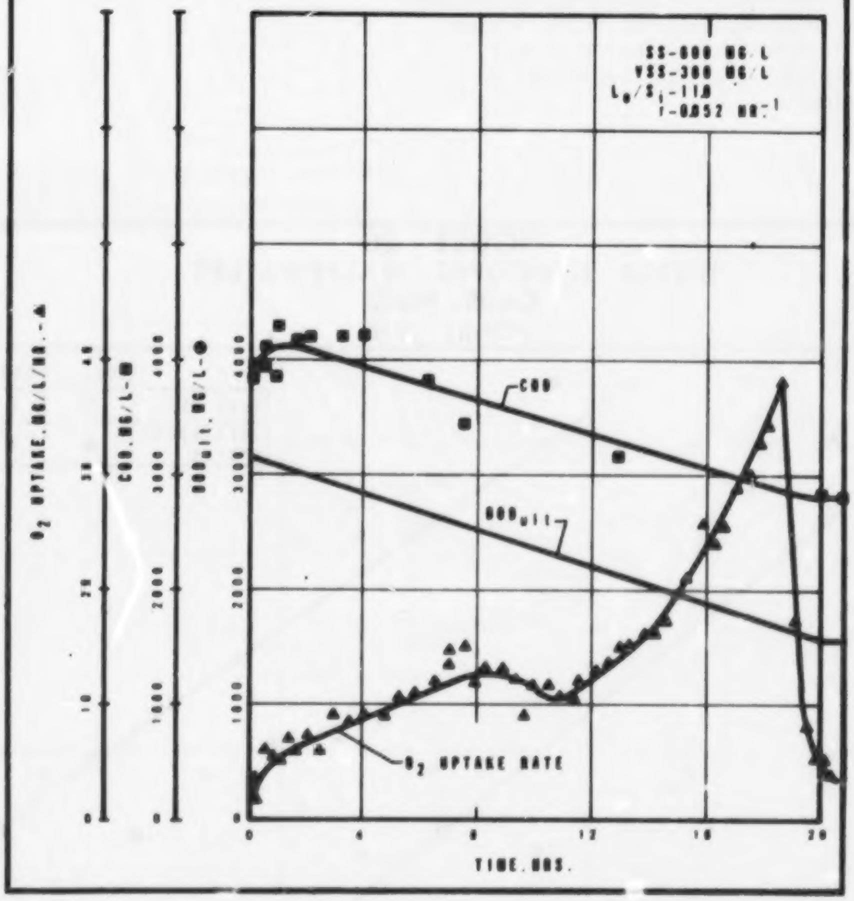


Figure 20 shows the correlation of transfer coefficients for BOD and COD to the food-to-microorganism ratio. The performance of the bench-scaled continuous system is shown also. The significant scatter reflects the variability of wastewater characteristics due to batch operations in manufacturing.

Case No. 3

The wastewater is from a textile finished operation (dyeing primarily). A scan of the four tubes of the "Tube Run" (Figures 21, 22, 23, 24) reveal the following:

a The oxygen consumption follows a characteristic pattern of rising to a peak, falling to a plateau and then decreasing to an endogenous level rather abruptly.

b Oxygen utilization extends beyond BOD removal.

c Energy oxygen increases as the mixed liquor suspended solids are increased.

FIGURE 20
TEXTILE DYESTUFFS WASTEWATERS
CASE No.2

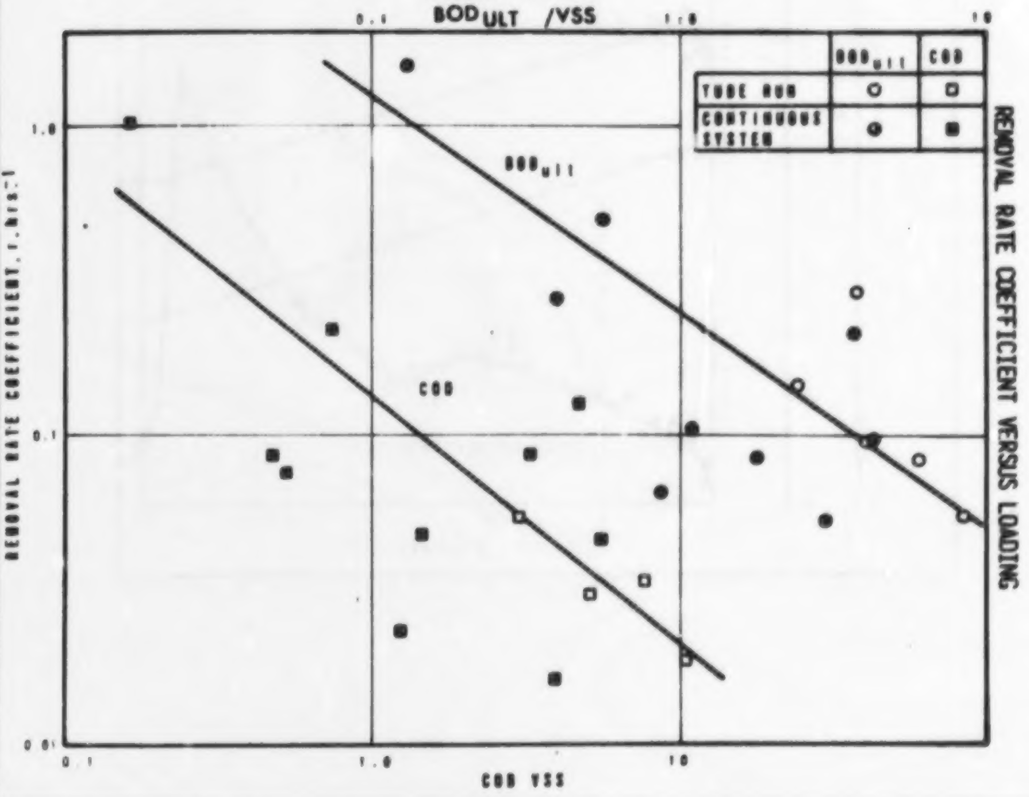


FIGURE 21
CASE No.3
TEXTILE FINISHING WASTEWATERS
TUBE 1

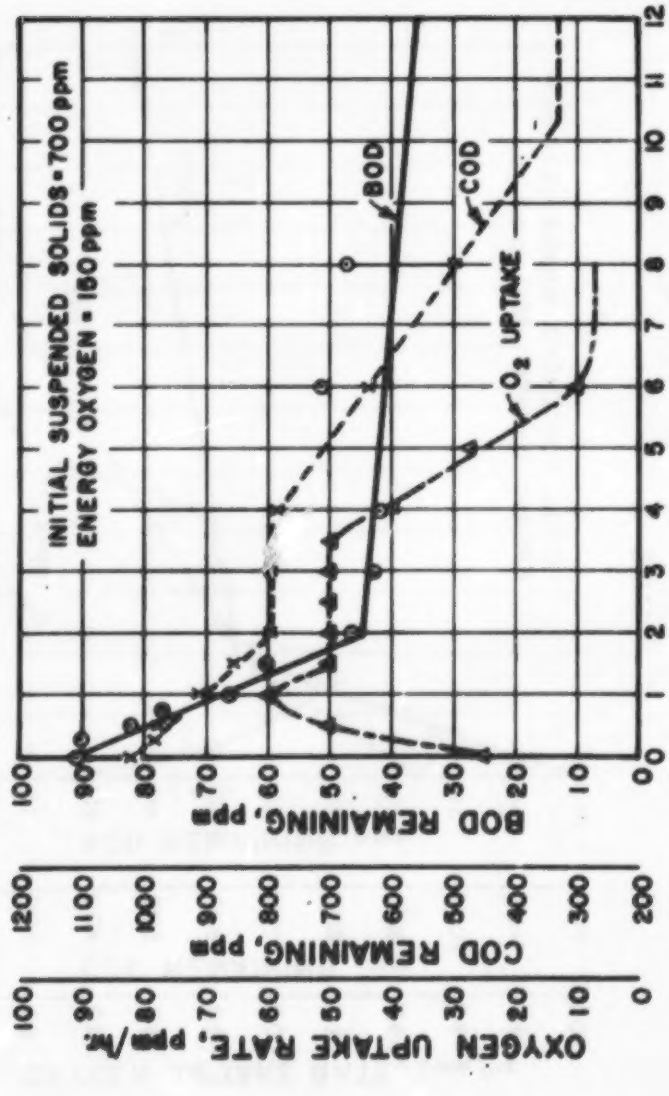


FIGURE 22
CASE No.3
TEXTILE FINISHING WASTEWATERS

TUBE 2

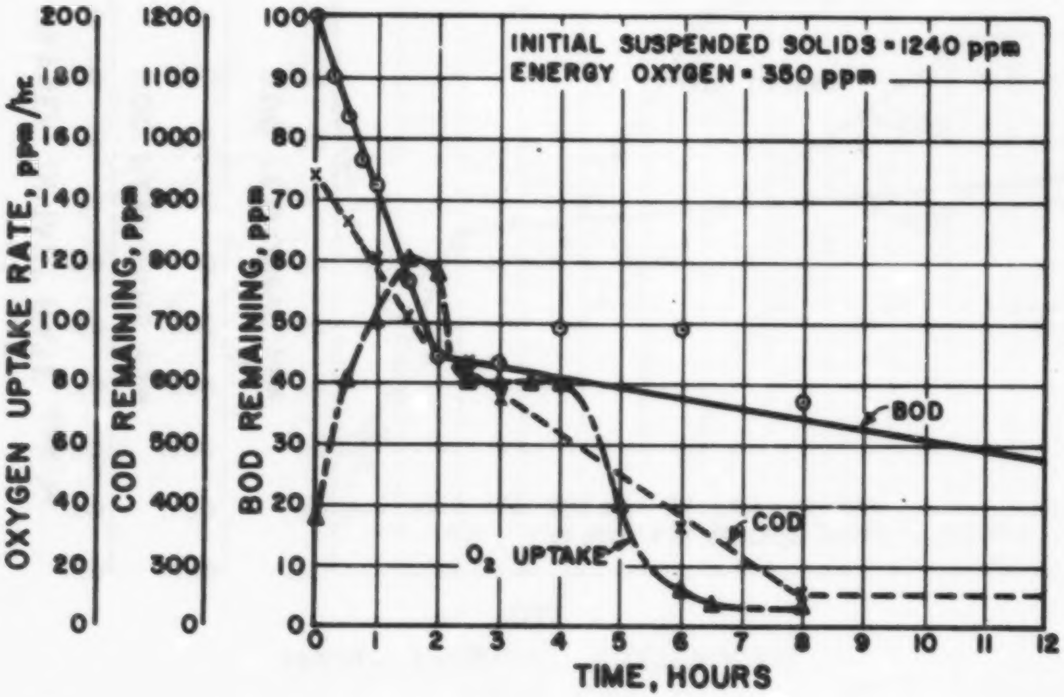


FIGURE 23
CASE No.3
TEXTILE FINISHING WASTEWATERS
TUBE 3

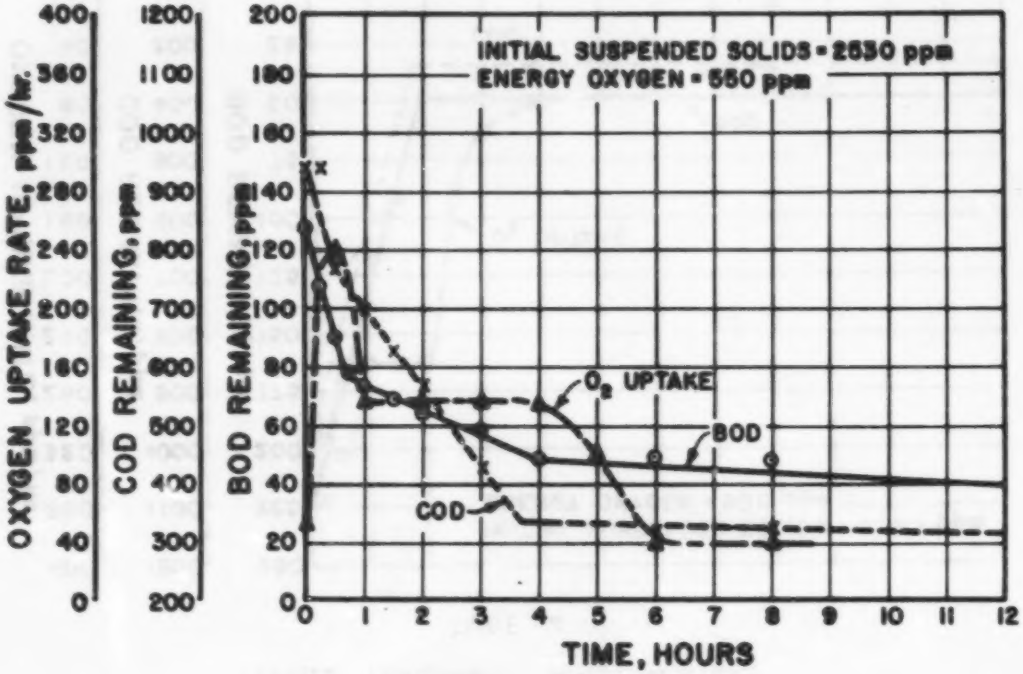
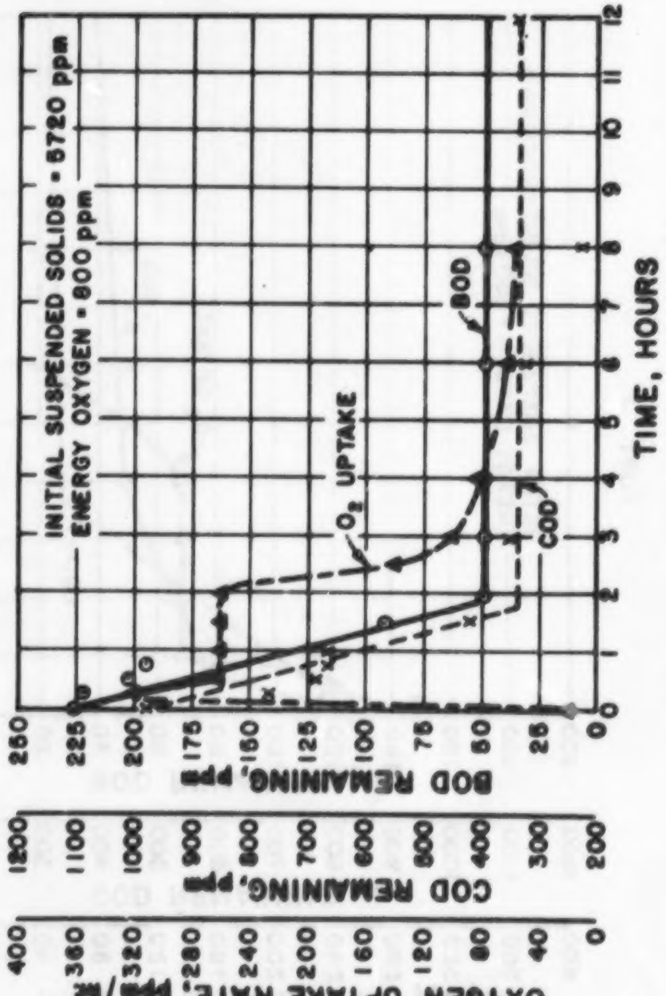


FIGURE 24

CASE No.3

TEXTILE FINISHING WASTEWATERS

TUBE 4

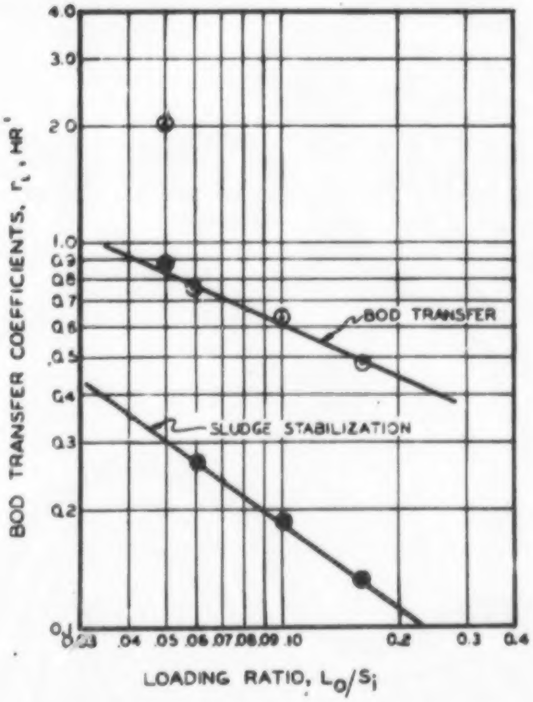


The pattern of energy oxygen is attributed to the accumulation of large dyestuff molecules in the activated sludge which do not in themselves provide enough energy for synthesis. When additional sources of energy are added to the system (a batch feed) a significant portion of the accumulated material enters into the energy-synthesis reactions. As a result, calculations based on the organic material in the feed do not adequately define the situation.

The correlation of the transfer and stabilization coefficients are shown in Figure 25. The activated sludge system was designed as a contact-stabilization process on the basis of the data. A single basin bench-scaled system performed in agreement with the slower stabilization kinetics.

FIGURE 25
CASE No.3
TEXTILE FINISHING WASTEWATERS

BOD TRANSFER RELATIONSHIPS
ACTIVATED SLUDGE TREATMENT



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This outline was prepared by Vernon T. Stack, Jr., Vice President, Research and Development Division, Roy F. Weston, Environmental Scientists and Engineers, West Chester, PA 19380.

BENCH-SCALE DETERMINATION OF WASTE TREATABILITY

I INTRODUCTION

A Biological treatment of domestic wastewaters by activated sludge has a long record. A good basic understanding is known although there is substantial disagreement on certain details.

B Industrial wastewaters may or may not follow the general rules established for domestic waste treatment. A large proportion of industrial wastes do follow patterns established for municipal wastewater treatment. The exceptions account for most treatability problems. These are the ones that require intensive laboratory investigation to seek effective control and treatment.

C The major items to be considered on problems wastes include:

1 Effects of microbiological adaptation on treatment.

2 Tolerable load characteristics under anticipated operating conditions.

  a food to organism ratio

  b concentration effects

  c hydraulic (time) effects

3 Solids production characteristics (nature and amount of process sludge)

4 Oxygen requirements and oxidation characteristics.

5 Effluent clarification characteristics.

6 Selection of analytical methods suitable to obtain the necessary information to rate performance, control the process, and interpret results.

7 Estimation of the effects of variations in the environment (biological, chemical, physical) on treatability.

8 Estimation of treatment efficiency, reliability and pertinent individual characteristics of the treatment process.

II FULL-SCALE VS. BENCH-SCALE OPERATION

A Although bench-scale studies cannot duplicate the conditions of a full-scale treatment plant, principles can be simulated. Applicability of bench-scale results depends upon the degree to which bench-scale operating conditions simulate those of anticipated full-scale operation.

B Pertinent factors for consideration include:

1 Proximity of inlets and outlets

2 Volume to container area ratio

3 Circulation and solids suspension

4 Oxygenation

5 Sludge return

6 Clarification

7 Flow and feed characteristics

8 Cleanup and maintenance problems

B2, 3, and 4 are particularly difficult problems and usually require careful extrapolation in scale-up. Comparison of bench and full scale results on a given waste helps in evaluation of results.

III CURRENT BENCH-SCALE APPARATUS

A The selected laboratory unit(1) (Figure 1) has a circle and cone design which provides a relatively large volume in relation to wetted surface area. Smooth surfaces tend to minimize sizewall attached growth. The cone bottom does not provide a large zone for solids lodgement at horizontal-vertical junctions. Location of the aerator at the bottom of the cone provides maximum turbulence in the limited zone of solids deposition to promote solids suspension and increase effective depth for contact of air and mixed liquor. Clarification is improved by the upflow of mixed liquor through the descending solids from prior entry, thus promoting agglomeration of solids. Sludge return is by gravity supplemented by an air lift, if necessary. The unit is relatively free of mechanical problems and easy to maintain for sustained operations. The unit is not intended to duplicate full-scale operation but it is useful for estimation of the possible treatability, likely problems, and development of methodology in analysis and operation.

B Feed rates controlled by the air inlet vacuum release provide for an unrestricted wastewater feed line and provisions for quantitative shock loading or any desired feed sequence depending upon anticipated plant flow characteristics.

IV OPERATION SCHEME

A Complete-mixing activated sludge is fed at varying rates approximating usual flow variations during the day. Usually about 75% of the 24 hr load is added within about 6 hours. Dose and starvation periods are checked for effects on performance.

B A given feed is usually added with municipal wastewater to provide trace nutrients and energy foods. Tap water dilution may be used to evaluate the need for accessory nutrients.

C Waste concentrations are varied to determine the maximum tolerable limit for sustained or short-time performance. Both random and controlled variation are useful.

D Organic load ratios (g COD/g MLVSS/day) are varied to determine permissible limits.

E Effects of detention time are checked at the optimum organic load ratio by varying waste concentration within acceptable limits.

F Adaptation characteristics are checked at various waste concentrations and load ratios to evaluate time requirements, treatment efficiency improvements, and performance characteristics.

G Sustained performance data are of major interest. Usually 4 to 8 weeks of continuous operation under specific conditions are used unless failure or poor performance occurs earlier. Short-time tests are of little value as an activated sludge may not show major effects of a feed change for one to two weeks.

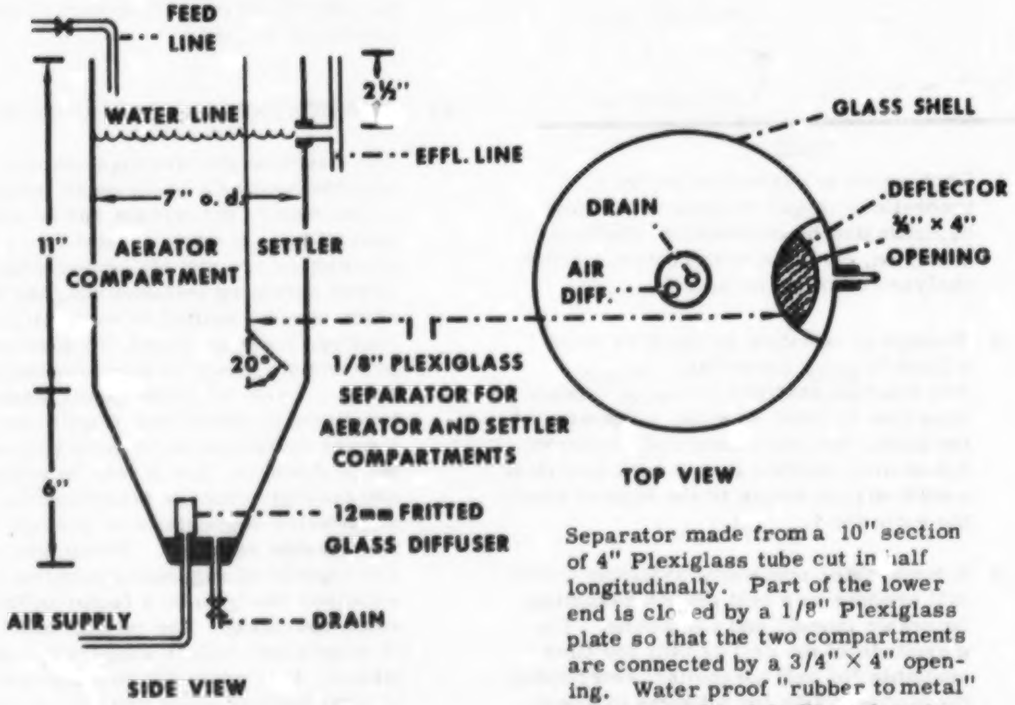
H Information is sought on the response to qualitative and quantitative(2) changes in loading, pH and temperature effects and other common variables depending upon the particular waste and its peculiarities under anticipated operating conditions.

V PERFORMANCE TESTING

A The first problem is to evaluate the common analytical procedures for their suitability on a particular waste. How reliable are the BOD, COD, suspended solids, chlorine demand, and other general procedures in evaluating waste characteristics or performance? What other tests are required to adequately define the system.

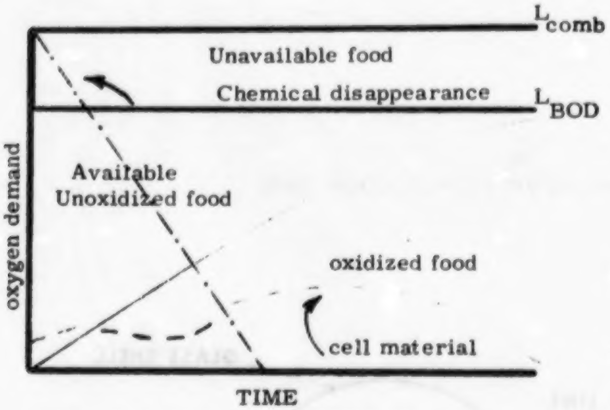
B Ettinger(3) describes a method of interrelating the basic factors of interest in bio-chemical oxidizability studies. The following diagram is adapted from his paper.

Figure 1. MODEL ACTIVATED SLUDGE UNIT


FEED LINE
2½"
WATER LINE
EFFL. LINE
7" o. d.
11"
AERATOR COMPARTMENT
SETTLER
20°
1/8" PLEXIGLASS SEPARATOR FOR AERATOR AND SETTLER COMPARTMENTS
6"
12mm FRITTED GLASS DIFFUSER
AIR SUPPLY
DRAIN
SIDE VIEW
GLASS SHELL
DEFLECTOR
¾" × 4" OPENING
DRAIN
AIR DIFF.
TOP VIEW

Separator made from a 10" section of 4" Plexiglass tube cut in half longitudinally. Part of the lower end is closed by a 1/8" Plexiglass plate so that the two compartments are connected by a 3/4" × 4" opening. Water proof "rubber to metal" cement used to join Plexiglass to glass.

7" o.d. Pyrex Shell 3/8" wall drawn to a cone.
Corning Glass Works
Spl. App. Div. Reference
No. D459051 - T140



1 Each waste is characterized by a theoretical oxygen demand which may be estimated by combustion, chemical oxidation, chemical composition, carbon analyzer or other means. (L_{comb})

2 Biological oxidation is likely to reach a limit (L_{BOD}) lower than L_{comb}. The fraction oxidized as L_{BOD} depends upon type of food, inocula, adaptation of the biota, and environmental conditions. Laboratory studies should seek practical conditions conducive to the highest possible ratio for L_{BOD}/L_{comb}.

3 A wastewater containing available foods will produce new cell growth assuming favorable inocula and conditions. The magnitude of the cell growth and time available for cell catabolism determines the sludge solids for ultimate disposal.

4 A major component in the waste stream may be followed by chemical analysis showing chemical disappearance, conversion to oxidation products, or cell material.

C A material balance obtained for carbon, nitrogen sulfur or other significant elements in the feed helps to evaluate results. What proportion of the feed appears as effluent or atmospheric carbon dioxide, nitrate, sulfate, or sludge solids.

D Will an effluent be likely to contain constituents contributing to objectionable odor, taste, color, nutrients, or other substances unduly degrading receiving water quality?

E Respiration rates, stripping of volatile feed constituents, biosorption, filterability or burnability of resulting solids are important information necessary to treatment plant design.

VI APPLICATION AND INTERPRETATION

A The bench-scale investigation will vary with the available background information on the waste, the stream and on allied operations. If waste treatability characteristics are closely comparable with known operating installations, the bench study may be limited to evaluation of loading, load variations, or process improvements based on pre-existing operations. A new or troublesome wastewater treatment problem may require an extensive investigation to ascertain what the problem is, how it may be controlled, and possibly process modifications or wastewater segregation to provide a manageable situation. Bench unit results are capable of suggesting problems or solutions likely to be a factor in full-scale operation. The results are "order of magnitude" values suggesting control limits. It is advisable to study operation of intermediate scale units to clarify scale-up problems whenever significant differences from usual operations are encountered.

B The bench-scale testing should closely simulate anticipated plant conditions. Batch test data on common wastes may be applicable to plant design after suitable extrapolation. Similar extrapolation on toxic wastes are likely to be misleading.

C Mixed wastes may respond satisfactorily to bench-scale results if toxicity is minor or organism adaptation is adequate. It may be necessary to check treatability of isolated wastes at their source or individual constituents to isolate the source of major difficulties. One low volume toxic waste component in a mixture may seriously distrupt treatment of the entire flow.

D A material balance of raw materials, processes, and products will estimate the nature and quantity of waste products from a manufacturing unit. We know treatability of a substantial number of chemicals common in wastewater.(4) It may be possible to materially shorten laboratory time by careful analysis of data such as this.

E Reliability and applicability of bench-scale research depends upon the skill and background of the analyst and his ability to operate bench tests in a manner that can be applied to plant test conditions. The symposium edited by McCabe and Eckenfelder(5) includes a large amount of information on biological treatability. Much remains to be learned about microbiological response which makes extrapolation dangerous. Proper experimental design minimizes the danger. A recent review(6) outlines oxidizability and treatability problems more extensively.

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This outline was prepared by F. J. Ludzack, Chemist, National Training Center, OWP, EPA, Cincinnati, OH 45268.

A VERSATILE ACTIVATED SLUDGE PILOT PLANT

- ITS DESIGN, CONSTRUCTION AND OPERATION

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Federal Water Pollution Control Administration
Department of Health, Education, and Welfare

A successful and consistently-operating pilot plant is an important phase of the total integrated research project. Jones (1) and Ludzack (2) have discussed in detail pilot plant methods, considerations, and problems. This paper is intended to go one step further and provide detailed directions for building and operating a versatile, experimental activated sludge pilot plant.

The pilot plant, designed for an average flow rate of 500 ml/min, has the following design objectives:

1. Service on unrelated projects for a number of years.
2. A degree of portability, allowing the unit to be transported into the field by conventional carriers such as small vans and panel or pick-up trucks.
3. Maintenance and operation time at a practical minimum.
4. Ability to operate, unattended, for periods of 16 to 24 hours.
5. Automatic representative sampling of the process streams.
6. Ability to vary the hydraulic and organic load in the approximation of actual operating experiences.
7. Ability to change from "plug" to "uniformly mixed" aeration flow patterns.
8. Ability to vary each unit's detention time independently of the flow rate.

In the following sections, the design, construction, and operation of the settlers, aeration tank, pumps, and samplers are discussed, supplemented by detailed construction drawings and a bill of materials.

Settlers:

It is impossible to retain in a pilot sedimentation unit the same surface loading, transverse liquid velocity, retention time, and geometric proportions that are encountered in full-scale practice. Practical operational considerations demand that the sludge be settled, concentrated, and drawn-off at one location. The settler design, shown in Figure 1, is a compromise of desired characteristics and practical operational and construction limitations. The unit is designed as a right rectangular pyramid with steep side walls to prevent solids "hang-up" and to enhance the solid-liquid separation phase.

Influent and effluent structures were designed to minimize stray current problems caused by the proximity of inlets and outlets. The influent nipple on the secondary settler has two purposes: (a) to bring the mixed liquid in at a low enough level to allow the sludge blanket to aid in the solid-liquid separation, and (b) to provide enough turbulence to prevent the settled solids from concentrating to such an extent that they undergo septicity and "bridge" a [illegible] the bottom of the unit, thus preventing the withdrawal of settled sludge. The overflow weir minimizes short-circuiting by assuring uniform draw-off of the settled decant. Because of the weir's adjustable height (Figure 2), the detention time and the surface overflow rate of the unit can be varied without changing the feed rate. When the unit is operated at design flows with a freeboard of 0.5 to 6.5 inches, the detention time in the settler varies from 94 to

45 minutes, while the surface overflow rate varies from 88 to 145 gpd/ft^2.

Aeration Tank:

In aeration tank design the most important variable is retention time or aeration tankage. The pilot plant aeration unit must be capable of maintaining the mixed liquor in suspension, achieving and maintaining dissolved oxygen concentrations comparable to full scale installation, and minimizing short-circuiting.

The aeration tank design is shown in Figures 3 and 4. The tank is spearated into six compartments or chambers by interior baffling; has an over-under, left-right flow pattern; and is liberally filleted in each compartment. Based on a design flow of 500 ml/min, each aeration chamber has a retention time of approximately 60 minutes. By use of rubber stoppers in appropriate locations, the detention time of the unit can be varied from 1 to 6 hours. The effluent structure is a rubber stopper, bored to hold a glass or plastic connecting tee with its apex arm sawed off at the stopper's interior face. To simulate plug flow or completely mixed flow, the baffles can be designed into the unit as permanent or removable (pressure fit) structures. If the baffles are removable, the other chambers not in use should be filled with water to equalize the hydrostatic pressures and prevent the mixed liquor from being forced into the adjacent inactive compartment. The purpose of the fillet pattern is to assure that the mixed liquor solids are kept in suspension by providing an incremental longitudinal roll. The diffusers are inserted through rubber stoppers and bent in such a manner that their heads lie against the forward bottom fillet in the approximate center of the tank.

The construction of the air supply header is described in the bill of materials (Table I). Air distribution nipples from the header are connected to the diffusers by flexible tubing. Screw clamps are used on each distribution line to allow external control of the air supplied to any given chamber. The total air supply (0 to 30 scfm) is supplied and crudely controlled by a rotometer. The diffusers are made from polyethylene instead of the more conventional porous stone; experience has indicated that stone diffusers tend to clog more rapidly with biological growths, resulting in larger bubbles and poorer mixing.

Sampler:

The automatic sampler is shown in Figures 5 and 6. The sampler is used to take semi-continuous aliquots of the influent, primary, and final effluent and to waste the return activated sludge at a uniform rate. Samples are collected by briefly diverting the process stream by a solenoid-valve, time-switch arrangement. The time of diversion can be set by the operator to assure collection of a representative sample.

Materials:

Materials for pilot plant construction vary, depending upon the size of the unit. Plexiglass was selected as the basic construction material because of durability and weight and ease of construction, modification, and repair. All main joints are screwed and bonded with a mixture of plexiglass shavings and dichloroethane; less critical connections are bonded only.

Persitaltic Pumps:

The peristaltic pump is shown in Figures 7 and 8. As does the Brittingham pump (3), it eliminates excessive fatigue in the flexible rubber tubing by use of four greased rollers instead of a stationary track. Collars are made with glass or plastic connecting tubes secured to the flexible tubing by copper wire. The tubing is slipped through the slot in the tube holder with a washer so that the tube collar rests against the support.

Pump delivery is controlled by the roller or shaft spacing, rpm, tube bore, tube-wall thickness, tubing tension, and whether the hydraulic head on the pump is positive or negative. Under a positive head, the pump provides a controlled syphon and serves as a metering pump; by adjusting the tension in the tubing, a wide range of flow rates can be achieved. With a negative head, the pump has a limited operating range for a given tube diameter; it acts as a piston pump, and flow rates can be estimated on the assumption that the distance between adjacent rollers is the "stroke" and the tube bore is the pump diameter. Since the tube is collapsed at the rollers and the bore becomes smaller as the tube is stretched, the effective capacity of the pump will be less than the calculated value.

Because fatigue of the rubber tubing is roughly proportional to the tension on the tubing and the rpm of the spindle, rpm rates greater than 30 are rarely used. When the pumps operate continuously, the tubing specified for 15- and 30-rpm pumps usually needs to be changed every 14 and 7 days, respectively. Torque on the drive shaft in the motor limits the distance between opposite pump shafts on the spindle; the practical limit for these motors is approximately 3 inches.

The peristaltic pump is used on the pilot plant to supply the influent and to return the settled activated sludge to the aeration chamber. It is inexpensive, non-clogging, self-priming, and provides consistent operation with a minimum of maintenance.

Operation:

The domestic sewage used in the pilot plant is heavily diluted by infiltration and run-off. This weak sewage (ss = 80 mg/l and COD = 120 mg/l) is not necessarily a handicap in experimental studies (4). Acting as a carrier solution, the waste's organic concentration can be adjusted or held nearly constant, and experimental results can be correlated to other parameters besides changes in organic loading. A ground, emulsified fish food (Table II) provides a satisfactory organic supplement, with a consistency and reaction similar to normal strength domestic sewage (4) (5) (6) (7).

The supporting facilities for an earlier activated sludge pilot plant designed by McDermott have been previously described (4)(9). To summarize, once each day sewage is pumped to a 325-gallon storage tank, where it is allowed to settle, and the heavy solids are wasted by gravity. Then a predetermined amount of fish food, which has soaked overnight, is added. The intermittently-mixed storage tank feeds a continuously-mixed constant head tank by a solenoid-valve, time-switch arrangement.

The sewage in the constant-head tank is fed to the pilot plant through a system of three peristaltic pumps, which operate in parallel on 24-hour timers. With an appropriate pump operating and fish food feeding schedule (Table III), the unit receives a square wave hydraulic pattern and half the 24-hour COD load in 6 hours, which approximates actual municipal wastewater treatment experience.

Maintenance of the unit requires approximately two man hours per day. Daily operation entails (a) collecting sewage and adding fish food, (b) collecting samples and withdrawing settled primary sludge, (c) checking pump flow rates (usually the pumps exhibit a tolerance of ± 10 ml/min), and (d) cleaning the side walls weirs, and sampling ports to remove any adhered solids. The exposed metal surfaces, pumps, and movable parts should be greased or oiled weekly.

Summary:

The completed 500-ml/min activated sludge pilot plant is shown in Figures 9 and 10. Its design, construction, and operation have been discussed, supplemented by detailed design drawings and a bill of materials for the settlers, aeration tank, sampler, and peristaltic pump.

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8. Eckenfelder, W. W. and O'Connor, D. J., "Biological Waste Treatment." Pergamon Press, New York (1961).

9. Moore, W. A., McDermott, G. N., Post, M. A., Mandia, J. W., and Ettinger, M. B., "Effects of Chromium on the Activated Sludge Process." Jour. Water Pollution Control Federation, 33, 54 (1961).

TABLE I. BILL OF MATERIALS

ITEM	MATERIAL OR EQUIV. MANUFACTURE *	SIZE	QUANTITY	APPROX. TOTAL COST
A. Aeration Tank				
1. Plexiglass 3/8" Thick 1/2" " 1" "	Cadillac Plastic and Chemical Company 6710 Madison Road Cincinnati, Ohio 45227	Get actual requirement from final design	4"x8" 4"x8" 3"x4"	68.00 90.00 66.00
2. Tie Bars	Stainless Steel	1/4" Dia. x 15" Long	3	1.50
3. Washers	Stainless Steel	1/4" I.D.	6	.25
4. Nuts	Stainless Steel	1/4" I.D.	6	.25
5. Stoppers	Rubber Stoppers Fisher Specifications Solid Fisher Scientific Co.	14-130-5 or 5 1/2	13	1.00
6. Tee	Glass	1/2" Dia.	1	.25
7. Air Supply Header	Copper - 45" Long Starting 3" from one end - drill 1/16" dia. hole, drill 5 more holes at 7-7/8" spacing - braze one end - attach 1" copper nipples w/1/16" I.D. to each hole		1	5.00
8. Labpor Gas Dispersion Tubes	Chemical Rubber Co.	F-1269-18	6	6.90
9. Misc. Screws	--	--	--	1.00
B. Settlers - Primary & Secondary				
1. Plexiglass	See Aeration Tank	--	--	--
2. Plexiglass Tubing 3/16" I.D.	Same	12"	--	
3. 1" I	Aluminum	19"	2	3.00
4. Wing Nuts	Aluminum	1/4" I.D.	8	.40
5. 1/4" Dia. Threaded Rod	Stainless Steel	8-1/2" Long	4	2.00
6. Misc. Screws	--	--	--	1.00

ITEM	MATERIAL OR EQUIV. MANUFACTURE	SIZE	QUANTITY	APPROX. TOTAL COST
C. Peristaltic Pump				
1. Induction Synchronous Geared Motor 115V, 60 Cycle 40°C Rise	Merkle-Korff Gear Company 213 N. Morgan St. Chicago, Ill.	Model BF 4215SAS Available in rpm range from 1 to 300	1	29.20
2. Motor Base Plate	Aluminum	1-1/2" x 3/8" x 1/2"	1	.45
3. Flexible Coupling	Aluminum		1	.50
4. Drive Shaft	Stainless Steel - Drill Rod	1/2" Dia. x 4-3/4" Long	1	.25
5. Spacer	Aluminum	1/2" I.D.	1	.05
6. Bearing	Oilite Bronze	1/2" I.D.	2	.10
7. Bearing	Oilite Bronze	1/4" I.D.	8	.50
8. Collar	Steel	1/4" I.D.	8	1.20
9. Collar	Steel	1/2" I.D.	1	.20
10. Pump Shaft	Stainless Steel - Drill Rod	1/4" Dia. x 2" Long	4	.20
11. Spindle	Aluminum	3-3/4" Oid. Rod	1	.90
12. Channel Mount	Aluminum	5" x 1-3/4" x 3/16" - 8-1/2" Long	1	1.00
13. Tube Holder	Aluminum Bar	2" x 6" x 3/16"	1	.30
14. Tension Adjuster Nut	--	5/8" Oid. x 1-1/2" Long, 1/2" I.D.	1	.25
15. Switch SI	SPST Toggle Switch	--	1	.40
16. Cord & Plug	6 ft. - 3 wire cord & grounding plug	--	1	.50
17. Misc. Bolts, Screws and Nuts	--	--		.25
D. Sampler				
1. Guardian Industrial Solenoid, 115V A.C.-Continuous	Mytronic Company 2145 Florence Ave. Cincinnati, Ohio 45206	12	1	4.25

ITEM	MATERIAL OR EQUIV. MANUFACTURE	SIZE	QUANTITY	APPROX. TOTAL COST
Plexiglass	Use scraps from unit construction	--	--	--
Misc. Parts (nuts, bolts, screws, springs, Al. Plates)	--	--	--	.25
Cord & Plug	6 ft. - 3 wire cord & grounding plug	--	--	.50
Miscellaneous				
Gear Rack & Timer	Allied Electronics 100 N. Western Ave. Chicago, Ill.	78Z461 78Z450 Come in varying time increments (1, 10, 20, 60, etc. min.)	1 1	1.75 18.75
Outlet Box	--	--	1	2.50
L for Unit Supports	Aluminum	--	--	30.00
Purina Trout Chow	--	Size No. 1	1-50 lb. bag	6.50
** Timers (24 hr.)	Holiday Appliance Timer - Mulley Products Co., 11 So. Morgan St. Chicago, Ill.	--	2	16.00
Flexible Tubing	Scimatco - Fisher Sci. Co. Rubber Tubing	14-150-5 (Dia. varies)	--	.10/ft.
Dichloroethane (Bonding Agent)	Supplier of Plexiglass	--	--	--

Man Hours Spent in Construction = 130
Labor Costs at 4.25/Hr. = $550.

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* Mention of company or product names is for identification purposes only and does not constitute an endorsement by the Federal Water Pollution Control Administration or the Department of Health, Education, and Welfare.

** Used to supply square wave feed

TABLE II. Fish Food Characteristics

% Volatile = 83

COD = 1220 mg/gm solids

% Nitrogen = 7

COD characteristics of 1 gram fish food homogenized in 1 liter of distilled water and allowed to settle for 1/2 hour:

Soluble COD = 25%

Nonsoluble COD = 33%

Settleable COD = 42%

TABLE III. Pilot Plant Operating Schedule

Time Period, hours	Flow Rate, ml/min	COD mg/l	COD Load, gm/hr	Comment
0 - 12	500	330	10	Change sewage in storage tank and add 200 gm fish food
12 - 18	250	330	5	--
18 - 24	750	580	26	Add 250 gm fish food
0 +				Repeat cycle

FIGURE 6

DISTRIBUTION OF INFLUENT & EFFLUENT PO_4-P
(MET-PRO PACKAGE PLANT)

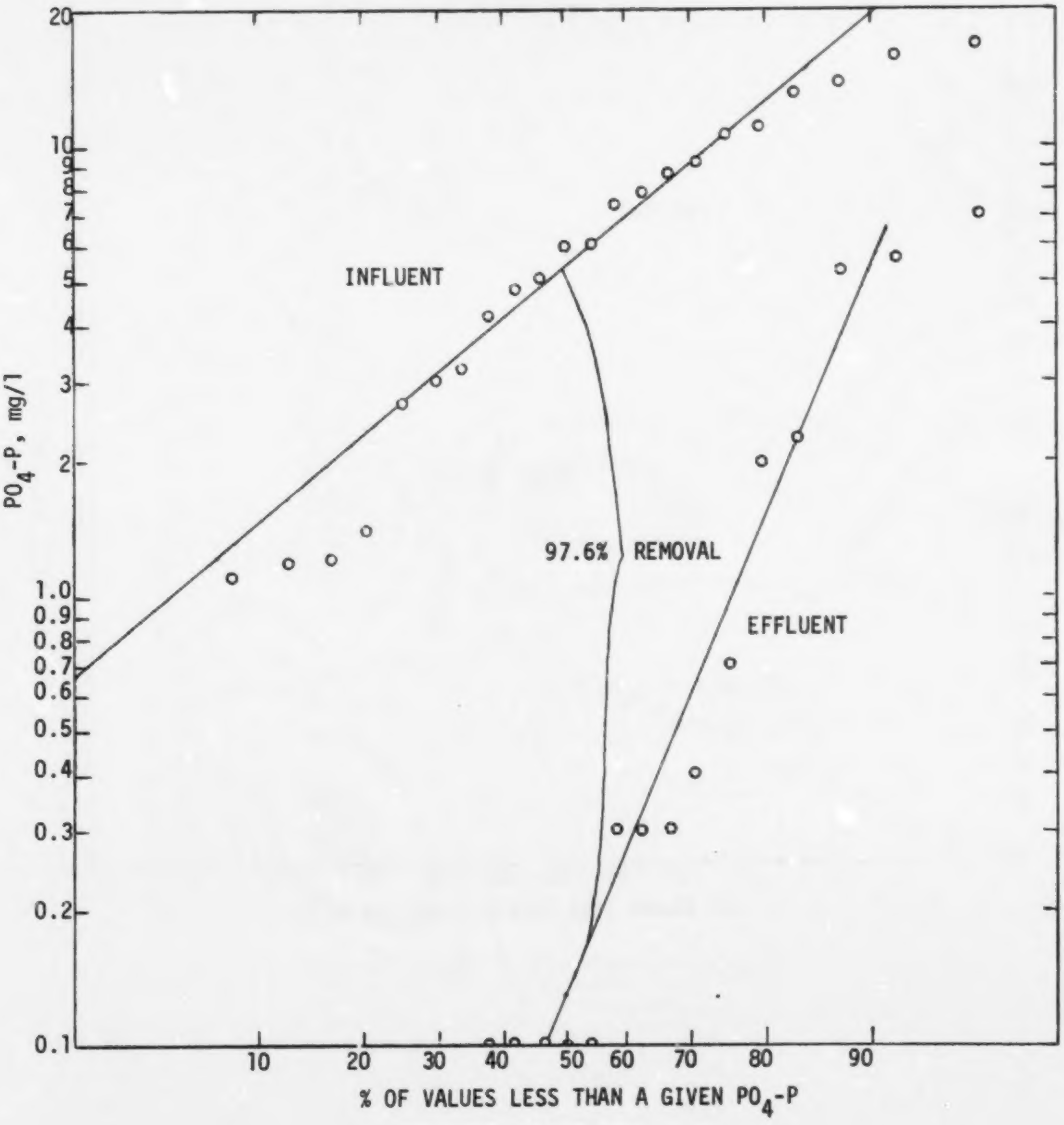


TABLE 4

CHEMICAL COSTS FOR THE MET-PRO PACKAGE PLANT (FWQA, CINCINNATI, OHIO)

	QUANTITY (1000 gal)	COST (per lb)	COST (per 1000 gal)
ALUMINUM SULFATE	2.51 lb	2.91¢	7.3¢
FERRIC SULFATE	2.51 lb	2.16¢	5.4¢
ACTIVATED CARBON			
*capacity = 0.05	1.67 lb	32¢	53.5¢
capacity = 0.75	1.25 lb	32¢	40.0¢
capacity - 1.00	0.84 lb	32¢	26.8¢

LOW: FERRIC SULFATE AND CARBON (cap. = 1.00) = 32.2¢

HIGH: ALUMINUM SULFATE AND CARBON (cap. = 0.50) = 60.8¢

*capacity of the carbon to remove organics in: lbs COD/lb carbon

TABLE 5

POLIOVIRUS I INACTIVATION AT 15°C IN THE MET-PRO PACKAGE PLANT (FWQA, CINCINNATI, OHIO)

RUN NO.	DISINFECTANT	CONCENTRATION mg/l		pH	KILL TIME (minutes)	
		DOSE	RESIDUAL		99%	99.9%
I	IODINE	5	3.0	7.3	16	25
	IODINE	1	0.2	7.5	84	150
	CHLORAMINE	15	14.9	7.3	25	60
II	IODINE	5	3.7	7.5	11	20
	IODINE	2	1.6	7.4	27	44
	CHLORAMINE	22	17.7	7.6	6	24

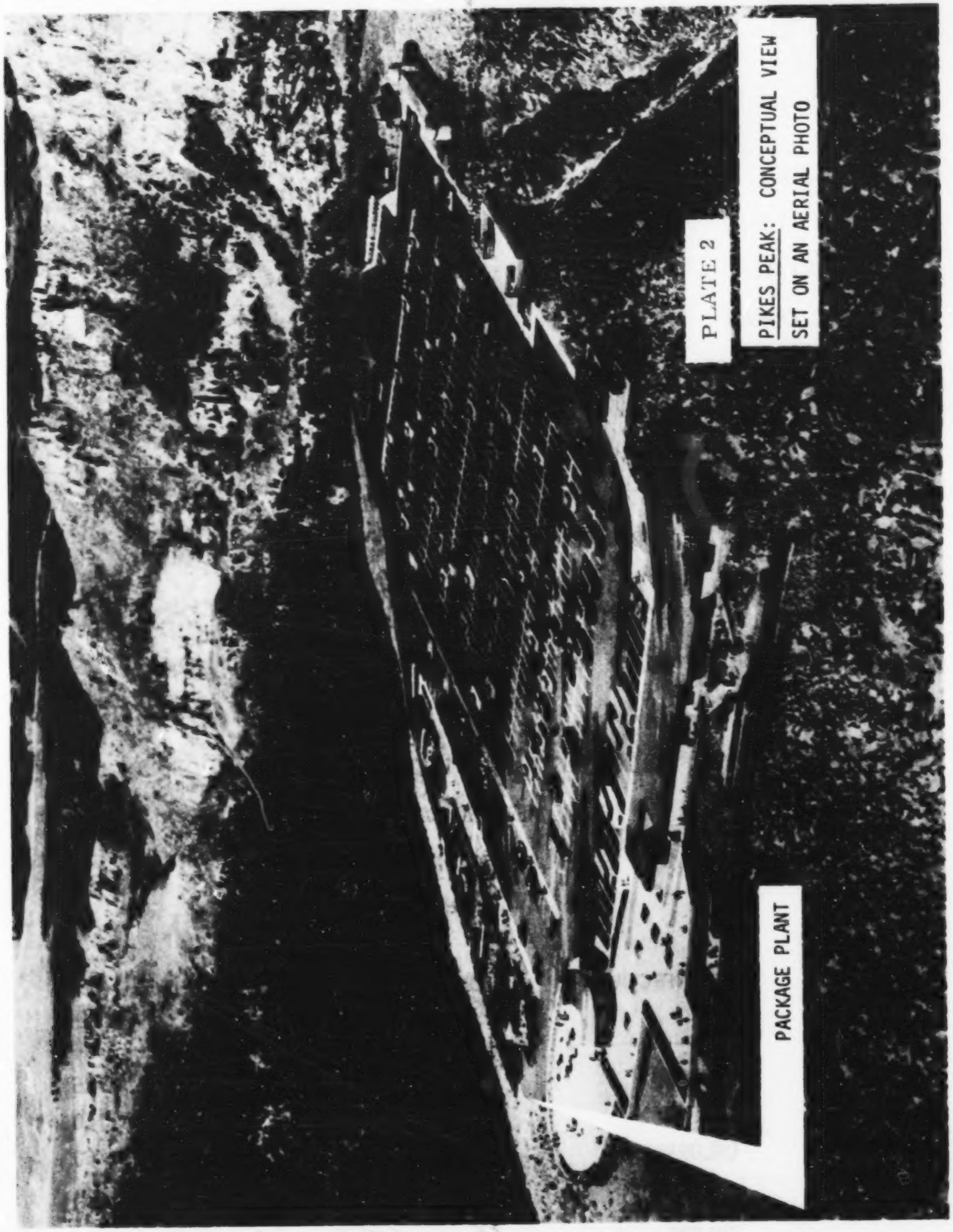

PACKAGE PLANT

PLATE 2

PIKES PEAK: CONCEPTUAL VIEW SET ON AN AERIAL PHOTO

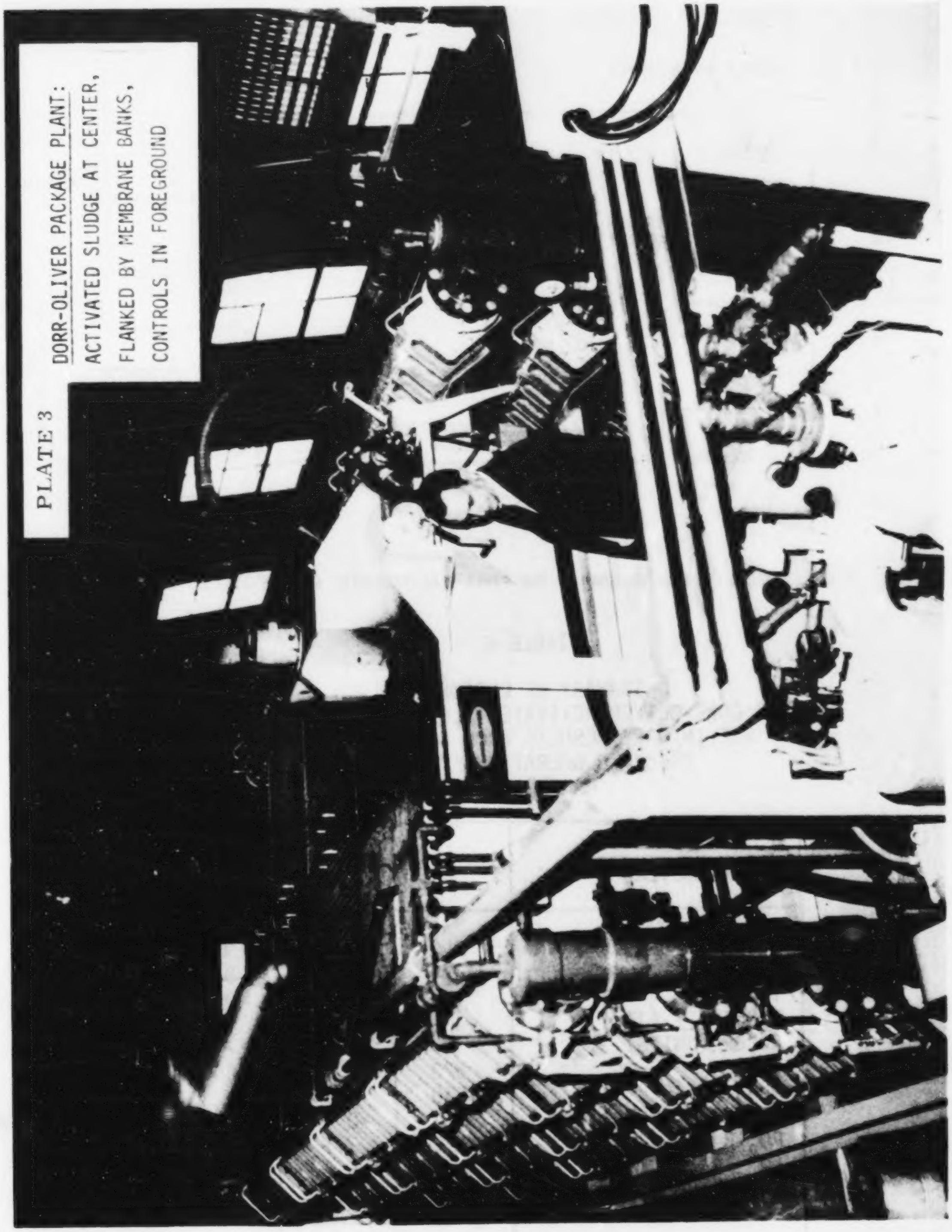


PLATE 3

DORR-OLIVER PACKAGE PLANT: ACTIVATED SLUDGE AT CENTER, FLANKED BY MEMBRANE BANKS, CONTROLS IN FOREGROUND

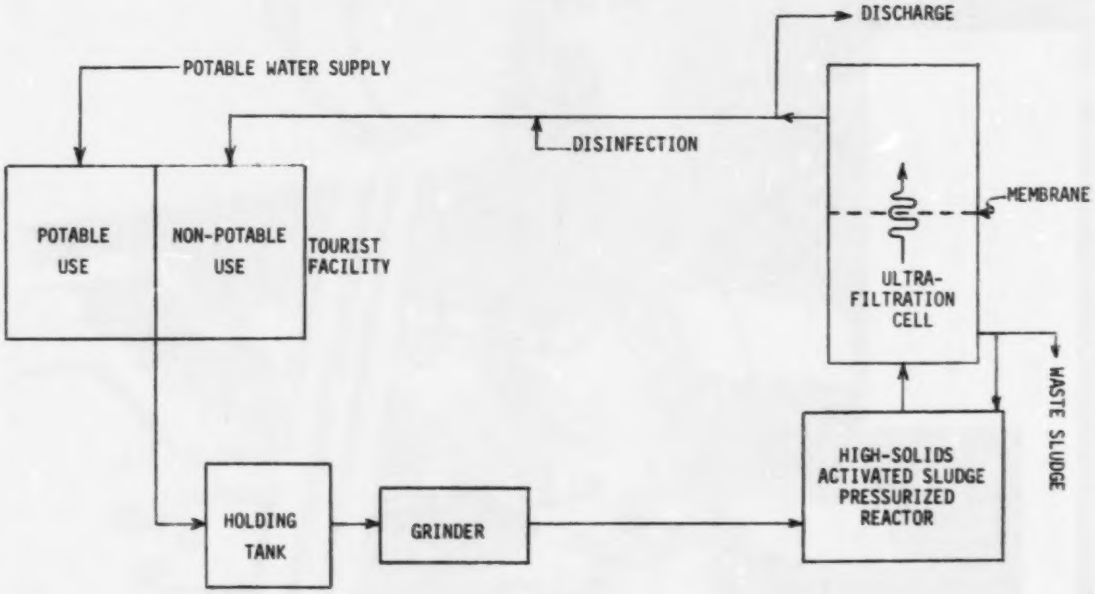

DISCHARGE
POTABLE WATER SUPPLY
DISINFECTION
MEMBRANE
POTABLE USE
NON-POTABLE USE
TOURIST FACILITY
ULTRA-FILTRATION CELL
WASTE SLUDGE
HIGH-SOLIDS ACTIVATED SLUDGE PRESSURIZED REACTOR
HOLDING TANK
GRINDER

Fig. 7. SCHEMATIC FLOW DIAGRAM OF THE PIKES PEAK TREATMENT & REUSE SYSTEM

TABLE 6

SUMMARY OF PERFORMANCE
OF THE DORR-OLIVER ACTIVATED SLUDGE-ULTRAFILTRATION PLANT
PRELIMINARY RESULTS FROM COLORADO SPRINGS
PRIOR TO OPERATION AT PIKES PEAK,
MARCH-JUNE, 1970

PARAMETER	INFLUENT mg/l	EFFLUENT mg/l	% REMOVAL
BOD	382	< 1	> 99
COD	678	20	97
TOC	192	7.5	96
TURBIDITY (JTU)	-	< 0.1	-
COLOR (UNITS)	-	28	-
TSS	323	0	100
MLSS	5510	-	-
COLIFORM (PER 100 ML)	-	0	100
PO_4-P	12.2	7.7	37
pH	7.02	6.62	-
THRESHOLD ODOR NUMBER	-	5.6	-
FLUX	10.1 GFD = 19,400 GPD		

30-16

FIGURE 8

DISTRIBUTION OF INFLUENT & EFFLUENT COD
FROM THE DORR-OLIVER AS-UF PLANT
(PRELIMINARY TRIAL)

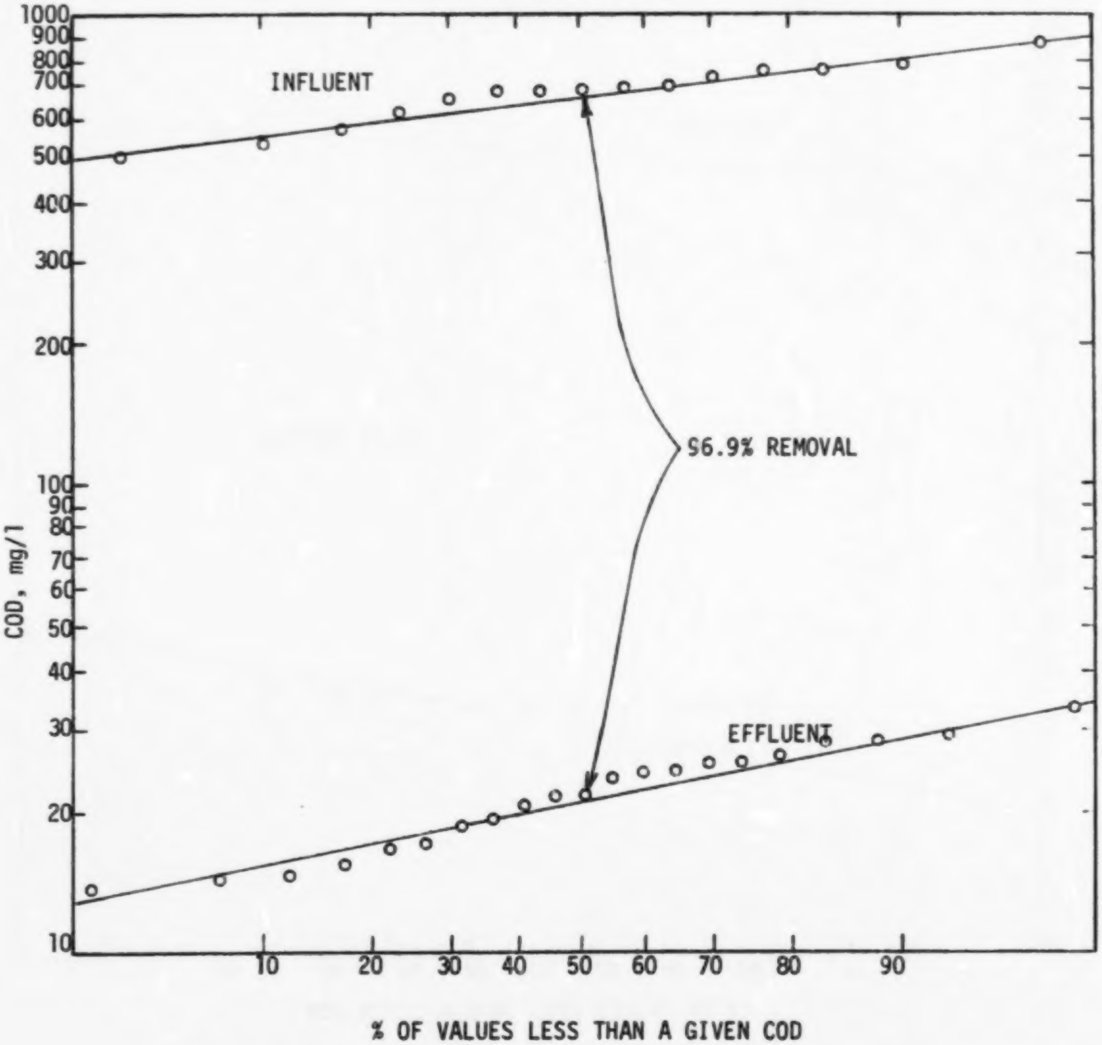
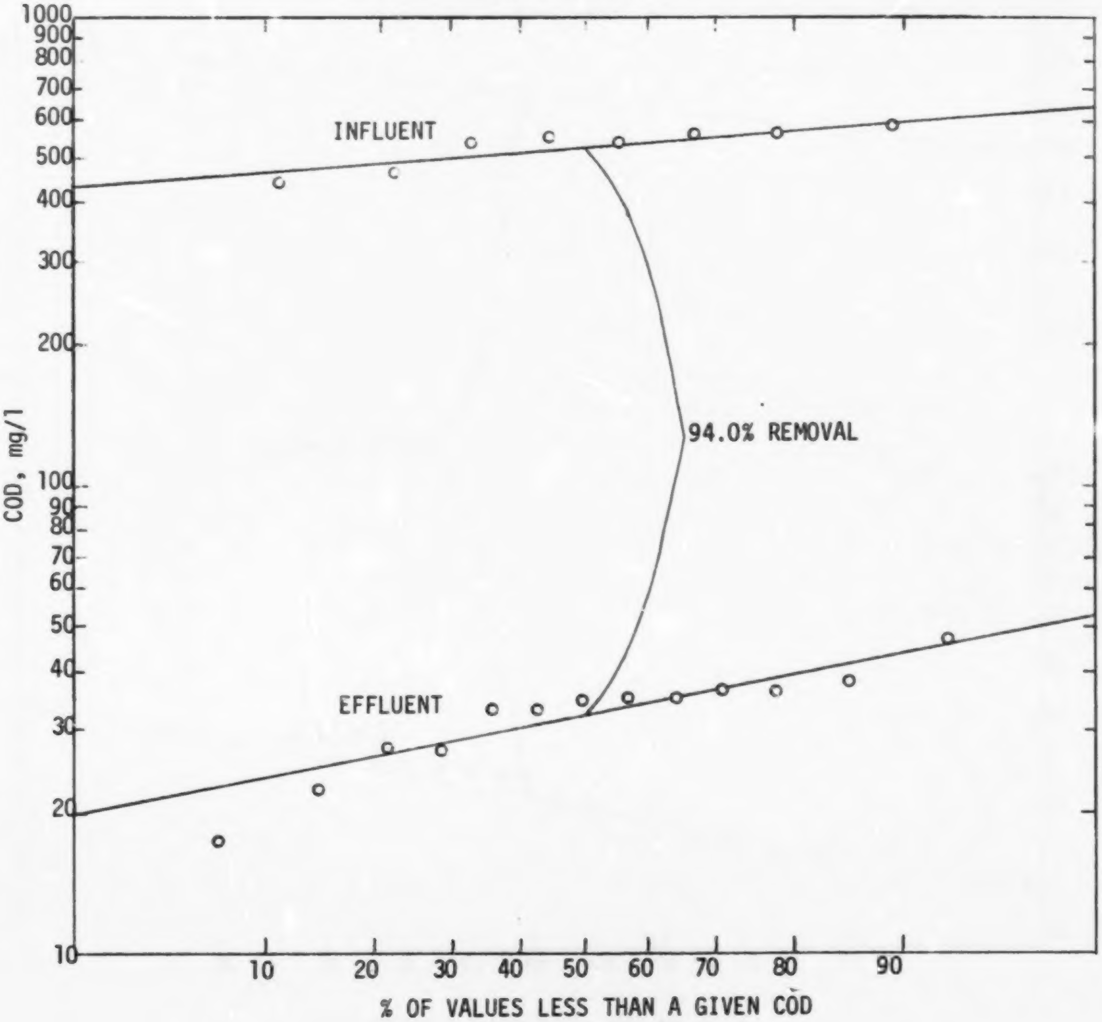


FIGURE 9

DISTRIBUTION OF INFLUENT & EFFLUENT COD
FROM THE DORR-OLIVER AS-UF PLANT
(PIKES PEAK)



30-18

FIGURE 10

DISTRIBUTION OF INFLUENT & EFFLUENT TURBIDITY
FROM THE DORR-OLIVER AS-UF PLANT
(PIKES PEAK)

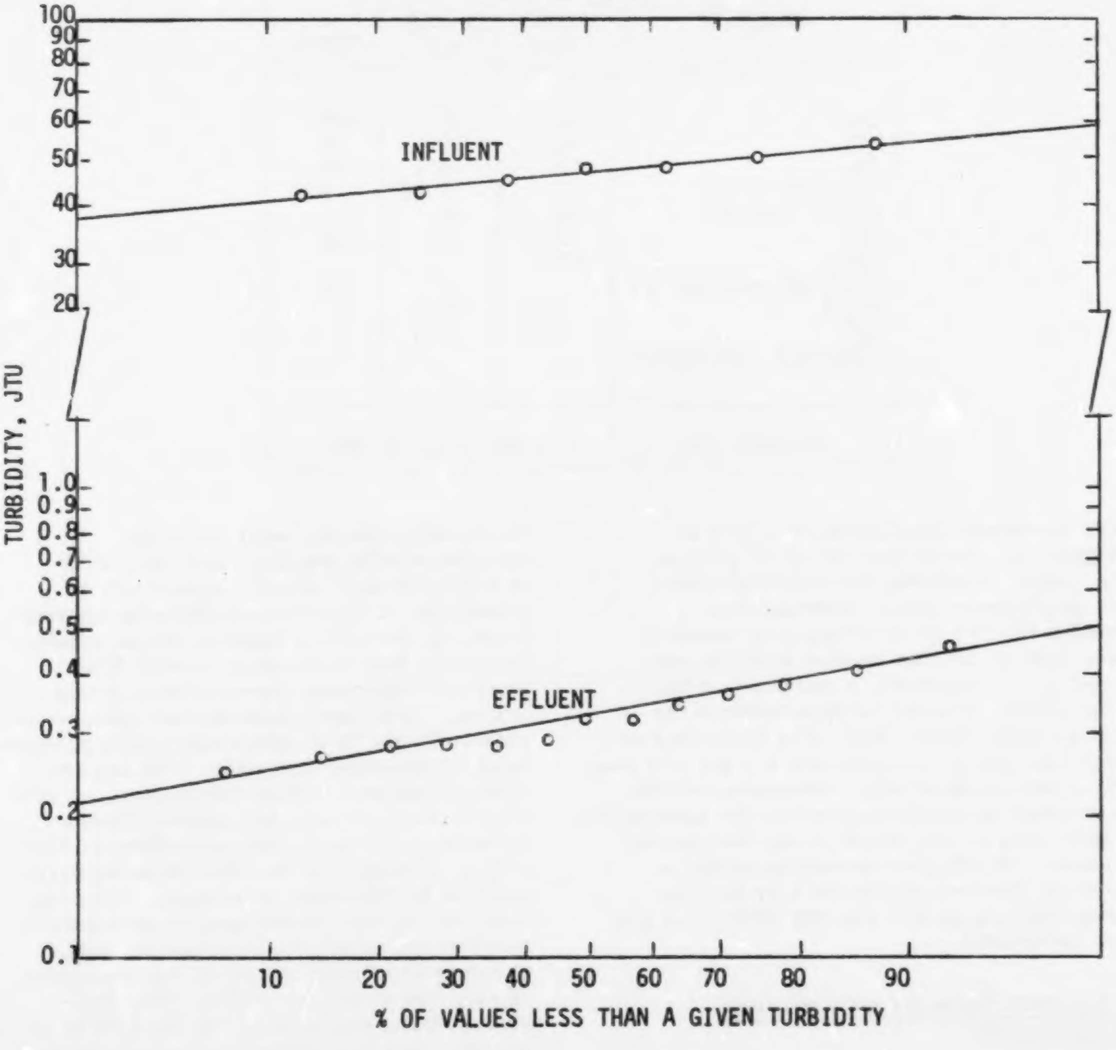


TABLE 7

SUMMARY OF PERFORMANCE
OF THE DORR-OLIVER ACTIVATED SLUDGE-ULTRAFILTRATION PLANT
OPERATIONS AT PIKES PEAK
AUGUST-SEPTEMBER, 1970

PARAMETER	INFLUENT mg/l	EFFLUENT mg/l	% REMOVAL
BOD	285	<1	>99
COD	547	32	94
TOC	136	6.6	95
TURBIDITY (JTU)	47	0.33	-
COLOR (UNITS)	320	40	-
TSS	129	0	100
MLSS	3954	-	-
COLIFORM (PER 100 ML)	-	0	100
PO_4-P	9.1	11.1	-
pH	7.9	5.9	-
THRESHOLD ODOR NUMBER	-	6	-
AVERAGE FLUX	11.0 GFD = 21,000 GPD		

The membrane flux decline is shown in Figure 11. The initial flux of 30 gfd was the result of washing the membrane after the preliminary trial. Although flux declined to 7-8 gfd in 20 days, no washing was done so the flux decline shown is misleading. If, however, it continued at the rate shown, it would be illustrated by the extrapolated dashed line. The flux would be about 2.5 gfd at 6 months and 1.5 gfd at 1 year. Six months coincidently represents both the membrane guarantee period and the approximate upper limit for the length of any one tourist season. Washing the membrane daily or several times weekly would keep the flux above the design flow (15,000 GPD = 7.8 gfd) for six months.

CLARIFICATION BY MOVING BED FILTRATION

An interesting concept which has applicability to treatment of small flows is the moving bed filter developed by Johns-Manville Corporation, Manville, New Jersey*. This device operates at hydraulic loading rates normally associated with deep bed rapid filters but at solids loadings usually applied only to clarifiers. It provides clarification superior to that achieved by a clarifier but in a space similar to that required by a rapid filter. Figure 12 illustrates the operation of this device. Raw waste is dosed with appropriate chemicals and flows into a tank which provides head for the filter operation. The sewage filters downward through the inclined packed bed of sand to a screened pipe and thence flows to a collector. Sewage solids and floc collect primarily on the filter face although some depth filtration is obtained. When the head loss exerted by the accumulated solids becomes excessive the sand bed is pushed upward and a cutter slices off the top layers of sand and suspended solids. The sand-sludge mixture is collected in the bottom of the head tank and is then pumped to a sand washer. Clean sand is returned to a hopper and eventually to the bottom of the sand bed.

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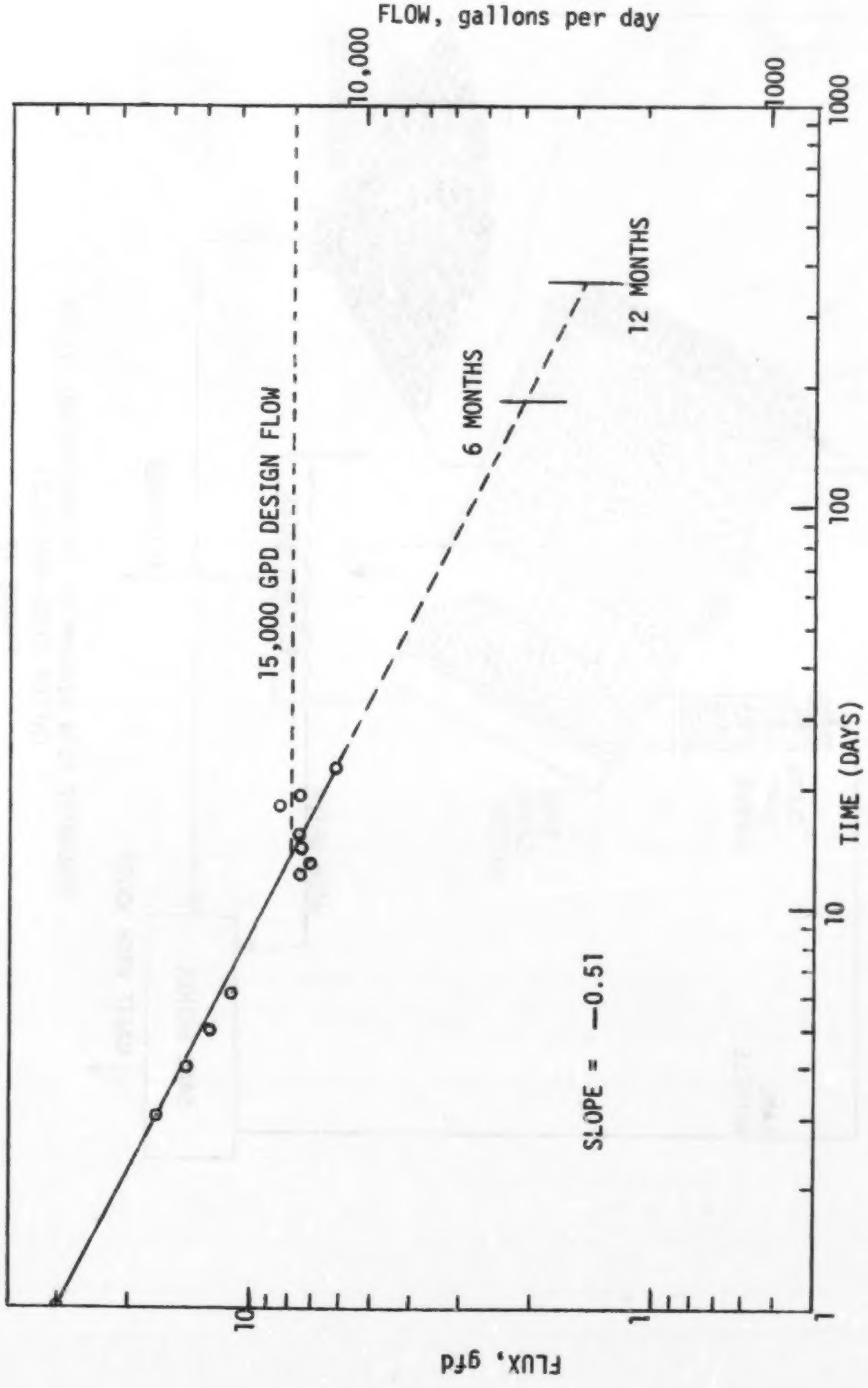
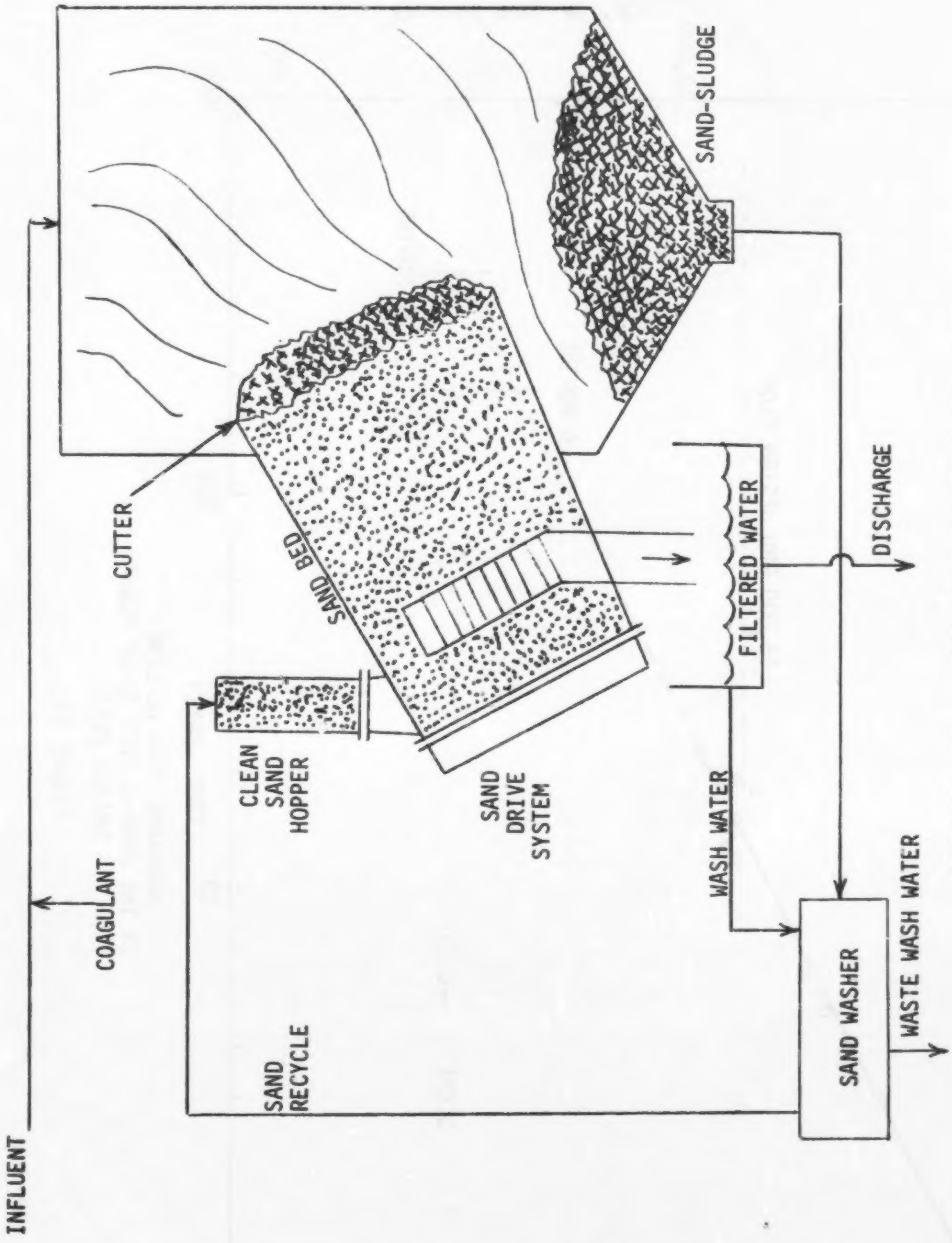
*Mention of commercial products does not imply endorsement by the Office of Water Programs, EPA.



MEMBRANE FLUX DECLINE
IN THE DORR-OLIVER AS-UF PLANT
(PIKES PEAK)

FIGURE 11

30-21


INFLUENT
COAGULANT
CUTTER
SAND BED
SAND-SLUDGE
CLEAN SAND HOPPER
SAND DRIVE SYSTEM
FILTERED WATER
DISCHARGE
WASH WATER
SAND WASHER
WASTE WASH WATER
SAND RECYCLE

SCHEMATIC FLOW DIAGRAM OF THE MOVING BED FILTER
(AFTER JOHNS-MANVILLE)
FIGURE 12

This system has been tested with raw sewage, primary effluent, and trickling filter effluent at the Bernards Township Sewage Treatment Plant. The pilot plant had a capacity of 10 gpm at the average hydraulic loading 2 gpm/sf. Alum and an anionic polyelectrolyte were used as the treatment chemicals. The results obtained in two weeks operation on raw sewage are given in Table 8. Excellent phosphorus, suspended solids, and BOD removals were obtained. In fact, the MBF produced treatment superior to that achieved by the Bernards Plant during this period (which consists of secondary treatment by trickling filter).

This work shall be expanded to other coagulants, and to evaluate the performance when powdered activated carbon is added to the feed to obtain additional organic removal. It is expected that the cost of once-used carbon required to insure organic carbon removal to the level of secondary treatment will be economically feasible for small flow application.

Johns-Manville estimates that the total cost of a 1 MGD plant is 12.0¢ per 1000 gallons. This estimate includes all operation, maintenance, chemicals (alum and polymer) and amortization of the capital expenditure of $264,000.

CLARIFICATION-CARBON-ULTRAFILTRATION TREATMENT

A potential small Advanced Waste Treatment plant is presently being evaluated in the laboratory and with a small prototype model by Oak Ridge National Laboratory. No significant amount of data has been collected yet, but the device is nonetheless worth mentioning.

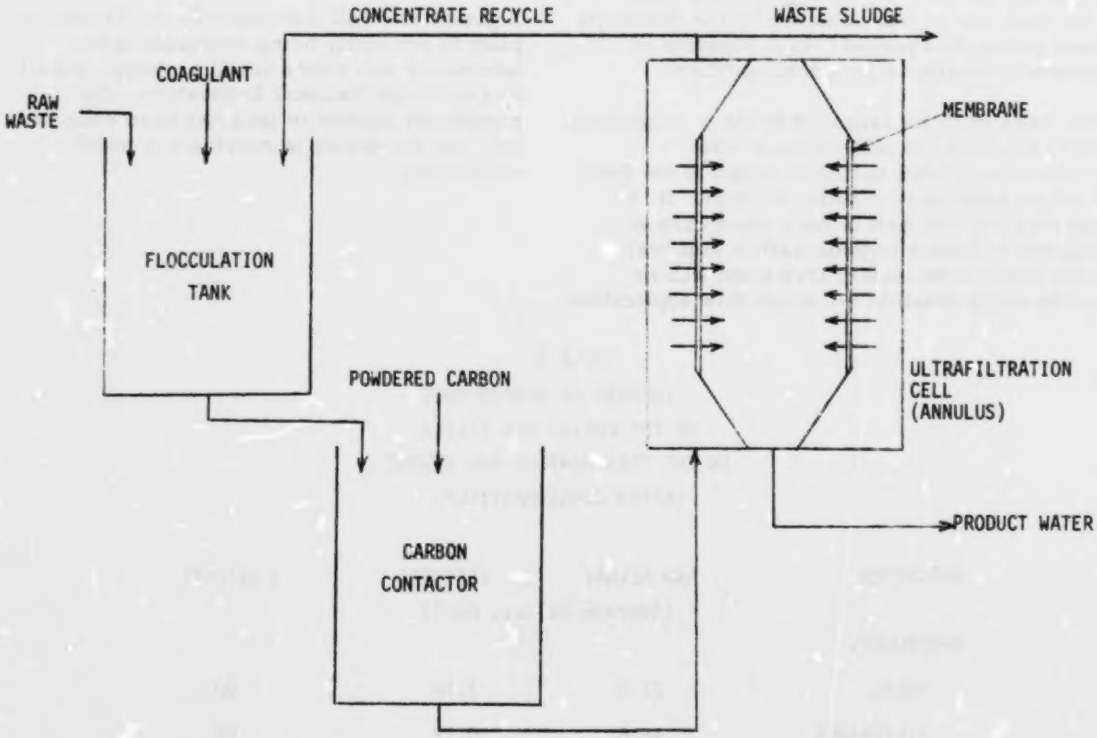
TABLE 8

SUMMARY OF PERFORMANCE
OF THE MOVING BED FILTER
IN THE TREATMENT OF RAW SEWAGE
(AFTER JOHNS-MANVILLE)

PARAMETER	RAW SEWAGE	MBF EFFLUENT	% REMOVAL
	(Average Values, mg/l)		
PHOSPHORUS			
TOTAL	21.5	2.16	90
FILTERABLE	18.6	0.79	96
ORTHO-	13.2	0.57	96
pH	7.2	7.0	--
TSS	156	27	83
TURBIDITY (JTU)	119	16	87
BOD	115	19	84

NOTE: COAGULATED WITH 200 mg/l ALUM AND ≈0.5 mg/l MAGNIFLOC 860A

This plant scheme consists of chemical clarification, powdered carbon contacting, and ultrafiltration separation of solids, as shown in Figure 13. The wastewater is contacted with coagulant as usual (so far, iron salts have been used, but lime is probably equally applicable) and flocculated, but no separation of floc is effected yet. A small dose of powdered activated carbon is added. The floc-carbon suspension is then pumped into the ultrafiltration cell where solids are separated. So far in lab tests, considerable fractions of organics as well as all of the solids are removed from the water with a membrane flux of about 100 gfd, or almost 10 times the IOFOR flux.


CONCENTRATE RECYCLE
WASTE SLUDGE
COAGULANT
RAW WASTE
MEMBRANE
FLOCCULATION TANK
POWDERED CARBON
ULTRAFILTRATION CELL (ANNULUS)
PRODUCT WATER
CARBON CONTACTOR

SCHEMATIC FLOW DIAGRAM OF A CLARIFICATION-POWDERED CARBON-ULTRAFILTRATION SYSTEM
(AFTER OAK RIDGE NATIONAL LABORATORY)
FIGURE 13

The IOPOR membrane used in the Dorr-Oliver plant is typical of conventional membranes. It is cast from a synthetic polymer on a rigid support in the form of parallel plates. Casting conditions as well as casting solution ingredients are closely controlled to assure the desired flux and rejection for the membrane.

The membrane in this plant is more unique. It is cast on a very coarse membrane support in the form of a firehose jacket on a stainless steel porous plate. The membrane itself is formed dynamically of a film of sewage constituents and filter-aid (here the coagulant). The dynamic forming process must also be closely watched since too heavy a membrane film will produce too tight a membrane. This in turn would reject a high fraction of the salts and produce a correspondingly lower flux (and greater flux decline). Given proper hydrodynamics, the membrane flux decline may be reasonable. Such a membrane has the advantage of negligible cost and ease of replacement, since it can be formed and destroyed in place. This unusual small Advanced Waste Treatment plant is very experimental to date, but holds promise of great versatility for a wide variety of pollutants.

SUMMARY

1 An urgent need exists for "small flow" treatment plants for a variety of situations.

2 Treatment systems based on Advanced Waste Treatment processes are far superior to biological package plants for small flow situations because of their stability of operation in the face of biologically toxic materials, and significant load variations. In addition, reuseable water if required can result from Advanced Waste Treatment processing.

3 Three general Advanced Waste Treatment based schemes of utility for "small flows" have been discussed. The three schemes involve a) clarification-carbon, b) ultrafiltration, c) chemical-biological processing.

4 Four specific systems which may have utility as "small flow" treatment plants have been described in some detail. Preliminary treatment performance from three is discussed.

5 Only one of these was specifically designed as a "small flow" plant and probably none are ideal for such a purpose.

6 Extensive development and testing will be conducted in the future to meet the needs for small flow plants.

REFERENCES

1 Bell, G.R., Libby, D.V. and Lordi, D.T. Phosphate Removal Using Chemical Coagulation and a Continuous Countercurrent Filtration Process. Final Report - FWQA Contract 14-12-154. June 1970.

2 Kreissl, J.F., Clark, S.E., Cohen, J.M. and Alter, A.J. Advanced Waste Treatment and Alaska's North Slope. Paper presented at the Cold Regions Engineering Symposium, 21st Alaska Science Conference, College, Alaska. August 1970.

3 Smith, R. A Rational System for Assigning Research and Development Priorities at the Advanced Waste Treatment Research Laboratory, Cincinnati, Ohio. Internal FWQA Report. September 1970.

This outline was prepared by I.J. Kugelman, W.A. Schwartz and J.M. Cohen, Physical and Chemical Treatment Research Program, Water Programs Operations, Cincinnati, OH 45268.

ANAEROBIC PROCESS PRINCIPLES

I INTRODUCTION

Anaerobic decomposition is employed for the treatment of organic sludges and concentrated organic industrial wastes. During the process volatile organic matter is degraded through successive steps to gaseous end products. These are primarily CO_2 and CH_4.(1) Since molecular oxygen is absent, the removal of methane and other reduced gases represents the BOD removal from waste under anaerobic digestion.

A Theory

1 Organic sludges go through two basic processes during the digestion process--liquefaction and gasification. Liquefaction occurs with extracellular enzymes which hydrolyze complex carbohydrates to simple sugars, proteins to peptides and amino acids and fats to glycerol and fatty acids.(1)

2 The ultimate end products of the liquefaction process are primarily volatile organic acids which are produced by "acid producing" strains of bacteria. The acids produced are primarily acetic, butyric and propionic.(1)

3 During gasification the end products of liquefaction are further broken down to gaseous end products. The principal components of this gaseous mixture are CO_2 and CH_4. During a well balanced digestion process, the processes of liquefaction and gasification occur simultaneously.

4 The degree to which the various substances present in sewage sludges and industrial wastes will be decomposed will depend on their chemical nature. Woody type material will result in approximately a 40 percent humus-like residue. Soluble organics are almost completely decomposed. With the exception of hydrocarbons, carbonaceous material is quantitatively converted to CH_4 and CO_2. Free fatty acids will undergo 80-90 percent destruction, ester fatty acids 65-85 percent and unsaponifiable matter 0-40 percent.(1)

5 It has been found convenient to describe the digestion process in three stages:

a Acid fermentation stage

b Acid regression stage

c Alkaline fermentation stage

The course of digestion of this three stage digestion process is shown graphically in Figure 1.

B Acid Fermentation Stage

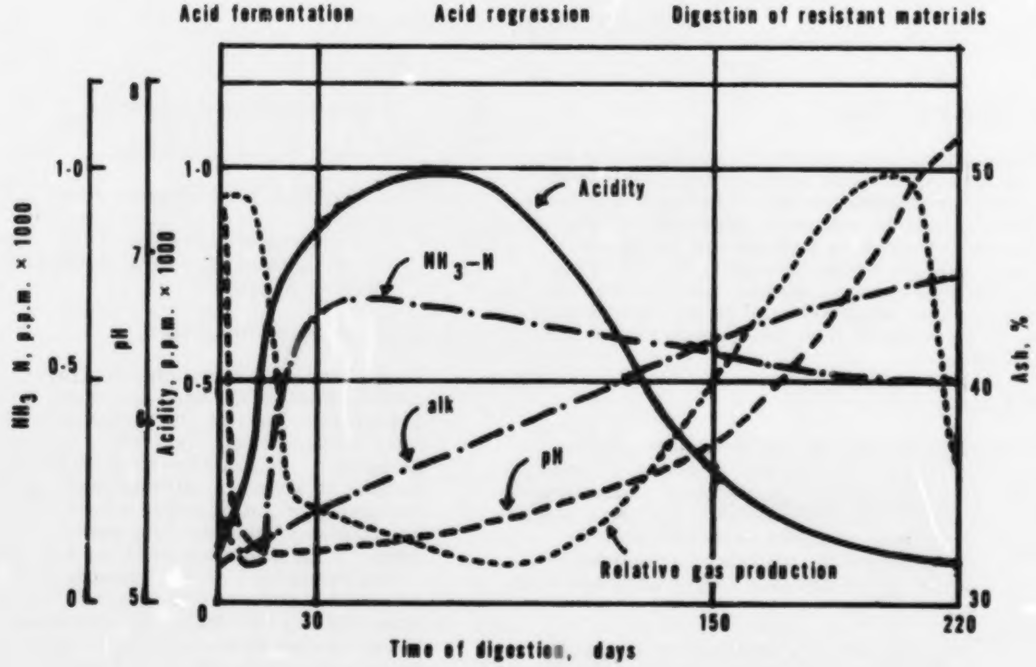
During the acid fermentation stage, carbohydrates (sugars, starches, etc.) are broken down to low molecular weight fatty acids, primarily acetic, butyric and propionic. This intensive acid production results in a drop in pH and leads to the formation of putrefactive odors.(1) The organisms primarily responsible for this stage of the digestion process are called "acid formers." They transform the waste into short chain fatty acids and are generally anaerobic or facultatively anaerobic. This group encompasses a large number of bacteria with a wide range of talents. As a rule, the acid formers are less sensitive to environmental factors than are the methane formers. Many of the acid formers are quite versatile as to substrate and end product while others are quite limited. Hence, in some cases, components of the waste may be taken to short fatty acids by a single organism, while in other cases, this transformation may require several organisms.

C Acid Regression Stage

During the acid regression stage, decomposition of organic acids and soluble nitrogenous compounds occurs resulting in the formation of ammonia, amines, acid carbonates and small quantities of CO_2, N_2, CH_4 and H_2. The pH will tend to increase during this stage. By-products resulting from acid regression will include H_2S, indole, skatol and mercaptans.(1)

D Alkaline Fermentation Stage

During the alkaline fermentation stage, destruction of celluloses and nitrogenous compounds occur. Low molecular weight organic acids produced during the earlier stages of the process are broken down to CO_2 and CH_4. The organisms primarily responsible for the process are the



Course of digestion of sewage solids (after Grune, 1958)

FIGURE 1

spore-forming anaerobes, the methane bacteria, and fat-splitting organisms. The methane bacteria are strict anaerobes, nonspore forming and require CO_2 as an hydrogen donator. These organisms require an inorganic nitrogen source (NH_3). The effective pH range for methane formation is pH 6.4-7.2.

E Gas Production

The gas produced from the digestion of sewage sludge and similar organic mixtures is composed primarily of CO_2 and CH_4 with small quantities of NH_3, H_2S, H_2, N_2 and O_2 present. Gas from a well-digesting sludge mixture will contain 25-35 percent CO_2 and 65-75 percent CH_4. A gas yield of 16-18 ft^3/lb of volatile matter destroyed can be expected from digesting sewage sludge. The following table from Buswell (1939) shows gas production from various sewage constituents.(1)

Material	CH_4 %	ft^3 of gas/lb decomposed
Fats	62-72	18-23
Scum	70-75	14-16
Grease	68	17
Crude fibre	45-50	13
Protein	73	12

II TYPE OF ANAEROBIC PROCESSES

A "Conventional" process generally used for treatment of concentrated wastes such as primary and secondary sludges such as at municipal sewage treatment plants.

B "Anaerobic contact process" designed to handle more dilute wastes and generally applied to specific industrial wastes.

C Process Units

1 Septic tanks

2 Imhoff tank

3 Conventional digesters

a Standard

b High rate(2)

4 Anaerobic contact

5 Anaerobic lagoons

III ENVIRONMENTAL FACTORS

A Biological - Nutrients(7)

1 Nitrogen and phosphorous - usually present in sufficient amounts in domestic wastes - may be required in some industrial wastes. Nitrogen must be added in NH_3 form, as NO_2, NO_3 forms are reduced and N_2 is evolved, hence lost.

2 Trace elements - Fe,(8) Mn, Mg, K, Ca, S, etc. - seldom a problem as waste usually contains sufficient amounts.

B Physical

1 Hydraulic loading

2 Temperature

a Mesophilic 85° to 100°F

b Thermophilic 120° to 135°F

3 Mixing

C Chemical

1 pH - range from about 6.6 to 7.6

2 Toxic materials

a Certain alkali and alkaline-earth are stimulatory at low levels and inhibitory at higher levels as shown in Table 1.(9)

b Ammonia toxicity

c Sulfide toxicity(10)

d Heavy metal toxicity(5, 11)

e Toxic organic materials

D Acclimation

1 Tolerance to certain cations can be increased by acclimation.(9)

IV OPERATION

A Control

1 Control of the pH of the anaerobic process depends on the maintenance of an adequate bicarbonate buffer system. A proper buffer system counteracts the acidity of the carbon dioxide as well as the acidity of the organic acids produced.

2 Use of ORP(4, 12)

3 Buswell(13) lists factors that interfere with digestion as:

a Sudden increase in feed

b Sudden change in pH of raw waste

c Sudden slug of inorganic material such as Zn, Cu, CN or "salts."

d Sudden temperature change

B Digester Seeding

1 Value of adding digested sludge to start digesters probably lies in production of favorable environmental conditions such as a suitable acid/alkalinity ratio as much as in the numbers of bacteria added.(14)

C Aids to Digestion

Distressed digestion can be attributed to a number of factors, all of which directly or indirectly alter the microbiological environment. In certain cases, a more favorable environment for these organisms can be provided by restoring the favorable environment by providing buffing alkalinity. Lime has been used and reported in many cases. Agricultural ammonia has been found to be successful in certain applications.(15) Buswell(13) suggests return of alkalinity in the sludge from secondary digestion.

V SUMMARY

A Anaerobic digestion processes are capable of treating greater amounts of organic matter in less space than aerobic.

B Sludge accumulation is less because of the greater influence of hydrolysis and lower rate of growth under anaerobic conditions.

C Environmental control major factor in effective operation.

D Methane produced represents a useful fuel and represents major BOD removal of growth.

Table 1. Stimulatory and Inhibitory Concentrations of Alkali and Alkaline-Earth Cations(5)

Concentrations in mg/l

Cation	Stimulatory	Moderately inhibitory	Strongly inhibitory
Sodium	100-200	3500-5500	8,000
Potassium	200-400	2500-4500	12,000
Calcium	100-200	2500-4500	8,000
Magnesium	75-150	1000-1500	3,000

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Table 2

METHODS OF PREDICTING METHANE PRODUCTION(12)

Empirical Equation:

$$C_nH_aO_b + (n - a/4 - b/2)\ H_2O$$

$$(n/2 - a/8 + b/4)\ CO_2 + (n/2 + a/8 - b/4)\ CH_4$$

1 Reactions not involving reduction of carbon dioxide

$$CH_3COOH \longrightarrow CO_2 + CH_4$$

$$4CH_3OH \longrightarrow 3CH_4 + 2H_2O$$

2 Reduction of carbon dioxide without net decrease

$$4HCOOH \longrightarrow CH_4 + 3CO_2 + 2H_2O$$

$$4CH_3CH_2COOH + 2H_2O \longrightarrow 7CH_4 + 5CO_2$$

3 Reduction and net decrease of carbon dioxide

$$4H_2 + CO_2 \longrightarrow CH_4 + 2H_2O$$

$$2CH_3CH_2OH + CO_2 \longrightarrow CH_4 + 2CH_3COOH$$

$$2CH_3(CH_2)_2CH_2OH + CO_2 \longrightarrow CH_4 + 2CH_3(CH_2)_2COOH$$

$$4CH_3CHOHCH_3 + CO_2 \longrightarrow CH_4 + 4CH_3{-}CO{-}CH_3 + 2H_2O$$

$$2CH_3(CH_2)_2COOH + CO_2 + 2H_2O \longrightarrow CH_4 + 4CH_3COOH$$

LIQUID TO SOLIDS TRANSFER

I INTRODUCTION

A The transfer of dispersed contaminents in used waters from the soluble or suspended particulate form into a solids concentrate or sludge that is removable from the main body of water is a major operation of wastewater renovation or treatment.

B Larger suspended particulates of a density sufficiently different from that of water tend to separate readily by floatation, sedimentation, centrifugation, screening and allied unit operations.

1 Soluble materials in water may not be effectively separated by the operations listed in B although some concentration on preformed particulates generally occurs.

2 Small sized suspended particulates of the colloidal size range also tend to remain dispersed for a substantial time interval unless their characteristics are altered to promote agglomeration into separable clusters.

C Conventional treatment of wastewaters include many mechanisms favoring the transfer of soluble or colloidal materials into a solids concentrate or sludge. The nature and rate of transfer varies with the component to be separated, its biological, chemical, and physical characteristics and conditions of the system at the time.

D Mechanisms favoring component concentration include:

1 Assimilation and conversion to cell mass.
2 Storage on or in cell mass.
3 Sorption on cell mass or other surfaces.
4 Mechanical entrapment within the sludge mass.
5 Filtration effects.
6 Bonding due to ion-exchange properties of the sludge and substrate.
7 Coagulation due to reactions among water and/or sludge components.
8 Clumping effects as a result of naturally formed polyelectrolytes in the system.
9 Surface interaction or contact effects of mixing.

E This outline considers the factors favoring transfer from the dispersed phase to the sludge concentrate that occur within 1 to 20 minutes of contact. Chemical addition for coagulation is not considered part of this topic.

II CHARACTERISTICS OF BOD REMOVAL IN CONVENTIONAL TREATMENT

A A very high rate of BOD removal was observed in the first few minutes of contact of wastewater and activated sludge (1). The removal exceeding growth rate of the sludge was considered as biosorption.

B The British classified BOD removal under 3 main headings (2)

a High initial removal and storage
b Removal of substrate in proportion to cell growth
c Endogenuous oxidation of cell mass.

It was observed that there was a progressive loss in clarifying power of the sludge after repeated feeding at 1/2 hour intervals. Feeding at 2 hour intervals of aeration maintained clarifying power. Excessive aeration time between feeding tended to cause some loss in clarifying power.

C Velz (3) and Stack (4) attributed most of the BOD removal in trickling filters to the short term removal with later stabilization of the retained materials in the attached slimes.

D Ullrich and Smith (5) upgraded an overloaded activated sludge plant by splitting the aeration facilities into biosorption and sludge stabilization compartments with the clarifier following the biosorption compartment. The net gain by removing the overflow and stabilizing more concentrated sludge permitted about two times the solids stabilization time in the same tankage.

E In general, there can be no BOD removal in biological processes without sludge growth. Short time removal is attributed to some form of storage where sludge accumulation exceeds the rate of conversion into cell mass. Subsequent contact of waste material before growth has resulted in formation of new active surface (or overgrowth of a lacy mass of active organisms) results in decreased removal. Sludge residence time for conventional activated sludge is sufficient for oxidation of a significant fraction of the previously grown cell mass.

F The contact stabilization, biosorption, step feed and other processes involving a contact of wastewater and sludge for 1/2 to 1 hour followed by clarification and reaeration of the concentrated sludge has become popular. Contact processes have many advantages:

1 Cost of aeration tankage may be reducted materially in a contact process because the bulk of the liquid is released after a relatively short contact period.

2 Aeration cost is likely to be reduced because the high respiratory activity of the contact zone is maintained by higher solids concentration in the regeneration zone. The greater driving force throughout aeration should favor greater oxygen transfer per unit air input or per HP/hr.

3 Separation of contact and sludge reaeration tankage makes it unlikely that a short term toxic inflow will poison all of the process sludge. The reservoir of side stream sludge may be used to reestablish good performance earlier.

4 The reservoir of regenerated sludge in a side stream makes it possible to closely match sludge return with process demand. More sludge may be returned as the load rises with the drawdown replaced after about one displacement of the contact and clarifier units. Side stream equilization decreases probabilities of returning an understabilized sludge to process after several hours of high loading.

G Contact processes also have certain limitations that may result in a lowered treatment efficiency.

1 Certain substances, such as soluble materials, may or may not be removed in the sludge to a degree sufficient for the requirements. Substances such as phenol and sugar are rapidly assimilated but they must be assimilated to be removed as sludge. Unassimilated residuals during the permitted contact time pass into the effluent.

2 The contact stage may favor higher concentrations of inflow components or more rapid changes than the sludge can accommodate in the adjustment time provided. The net result is a lower degree of overall removal.

3 If oxygen demand in the contact stage exceeds oxygen supply, the absence of DO produces a less effective treatment. Both solids capture and sludge stabilization capabilities are reduced by a DO deficiency; concurrently, more oxygen is needed to restore sludge capabilities for purification.

4 A contact treatment process may be selective in removal of specific fractions of the load because some materials rare removed more effectively than others. For example, linear alkolate sulfonate (LAS) was observed to have about 75% transfer to the sludge. More efficient removal generally is sought.

5 It may be expected that a contact stabilization process will not provide as much cleanup as a conventional or complete mix activated sludge given the same load and conditions.

III TESTING FOR CONTACT PROCESS FEASIBILITY

A A basic requirement for any treatability study should include observations of contact kinetics. The removal versus contact time and conditions for general and specific cleanup is important.

B The test may be performed in many different ways. The essentials include:

1 Completely mix a definite volume of influent of known concentration with a definite volume of sludge solids of known concentration. Do not try to homogenize the mixture.

2 At preselected intervals, i.e., 5, 15, 30 minutes and 1, 2, and 3 hours withdraw a portion of liquid from the agitated and aerated mixture.

3 Separate the withdrawn mixed sample of liquid and solids rapidly. Centrifugation is recommended. Settling or filtration is too slow. Do not use coagulants unless these are to be used in the intended operation.

4 Test the liquid fraction and compare with the influent characteristics and with a reference sample of sludge and tap water in the same proportions and sequence. The tap water is used to check sludge washout upon dilution. This may be very high on an unstabilized sludge.

5 Tests used on the clarified fraction depend upon treatment objectives and the particular substrate and situation. Both general and specific tests are advisable.

a BOD is usually advisable. Remember that the ultimate BOD is more important than any one point on a progression.

b COD usually is applicable to estimate first stage oxygen demand.

c Total Kjeldahl nitrogen (TKN) is important for second stage oxygen demand estimates (TKNx4.57).

d Total organic carbon (TOC) and total oxygen demand (TOD) from carbon hydrogen nitrogen and sulfur demand are quick and valid if instrumentation and capable personnel are available.

e Turbidity, clarity and/or suspended solids (SS) are important because effluent quality usually depends upon the discharged solids.

f More specific tests, such as ammonia phosphorus, surfactants, phenolics, sugars, cyanides, or other components are important in proportion to their significance in the influent and the situation.

g Sensory observations regarding visual appearance (scum, oily residues, particulates, color, emulsions) odor, taste, or anything else observed that may provide a cue to subsequent quality are important.

h It is important to check removal selectivity. Commonly particulate materials are removed more completely than soluble materials. There is a large variation in removability of different substrates depending upon chemical, physical, and biological characteristics.

IV INTERPRETATION OF RESULTS::

A The bench test provides information useful for design selection of process and identification of likely problems during later operation.

1 Information derived from it is no better than the efforts and capabilities put into it.

2 The test should be carefully designed in line with the situation, information needed, and requirements to be met.

3 Bench data are unlikely to be precisely transferable to full scale operation. The principles are transferable. It is important to test known situations on bench and full scale to provide cues on what is or is not transferable for unknown situations.

4 It frequently is necessary to test intermediate scale operations to evaluate effects of scale-up when the bench work indicates a problem that cannot be evaluated effectively in bench scale operations.

B Certain observations may be encountered in bench work on transfer kinetics that have a real effect upon subsequent choice.

1 Adaptation of the active sludge for a particular influent is important. Transfer of substrate to the solids concentrate may improve as the sludge organisms adapt to assimilation and retention of the substrate. It is not essential that the substrate be completely degraded within contact time. As long as it has been modified enough to hold it in or on the cell mass, or sludge, as a storage product, it may be removed in process. Phenolics in acceptable concentrations are removed effectively by trickling filtration and other short contact operations by adapted organisms.

2 Concentration of substrates during contact is very important. A given concentration of phenolics may be removed effectively upon short term contact with an adapted sludge. Double or trebled concentration of the same phenolics under similar operating routine may result in high concentrations in the effluent and possibly a damaged sludge.

3 Combinations of substrates may show results that are materially different from either one separately. A sludge capable of accepting 100 mg/liter of mineral oil emulsion and of phenol separately without significant damage and good transfer kinetics failed completely upon exposure to simultaneous application. The combination resulted in cell mass disruption with the production of a centrate having a milky physical form, a strong phenol odor and a COD much greater than that of the combined influent.

4 Accumulation of a given influent substrate having a low oxidation rate in the sludge may result in retrogression of transfer kinetics upon repeated application. A single application of mineral oil at 100 mg/liter is likely to be transferred effectively to the sludge mass with moderate effects upon performance. The same dose or smaller doses on reapplication may result in little transfer of oil when the sludge attains an oil concentration (dry basis) of about 5 to 10%. The mineral oil degradation rate in an aerobic system usually is sufficient to maintain activity if the influent concentration of oil generally is less than 10 mg/liter. More than this on a continuous loading basis may result in sludge performance losses.

5 Activity of the sludge as indicated by performance or respiratory oxygen use is fundamental. An overloaded or poorly regenerated sludge cannot perform as intended, either for contact or conventional operation.

6 A mixture of substrates may show large differences in removal kinetics depending upon individual characteristics. LAS showed about 75% transfer to solids upon initial contact, whereas other wastewater constituents were about 90% removed in less than 10 minutes contact. It required 3 to 5

hours aeration for LAS concentration in the liquid phase to be reduced from 3 to 1 mg/liter.

V SUMMARY AND CONCLUSIONS

A It is not advisable to assume that contact stabilization on other short contact processes will be suitable unless tests or operational history on similar wastes show that required specifications are likely to be met.

B It may be expected that longer aeration periods in mixed influent and sludge will provide better cleanup of influent contaminents than a contact process under similar conditions and loading. Effluents may be upgraded by longer contact time, recycle, two stage operation or better operational control.

C Higher solids in relation to loading tend to increase removal and favor stabilization if DO can be maintained. Higher solids are likely to function as a trade-off for reduced time within certain limitations.

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SLUDGE DISPOSAL BY LANDSPREADING

I INTRODUCTION

A Wastes removed from water must be disposed of in air, water, or land. Recycling of some components may delay disposal.

B Fresh water is no longer acceptable as a receptacle for wastes.

C Ocean disposal of organic waste and some chemicals is a questionable practice.

D For many cities and towns spreading liquid wastewater sludge on the surface of the land is the simplest, most inexpensive method of sludge disposal. It conserves plant nutrients and organic matter for utilization by plants.

E There are potential hazards involved with improper landspreading practices. Recycling nutrients and water in soils is beneficial if correctly applied. Certain hazardous or damaging materials accompanying the nutrients are serious problems.

II HISTORY

A Disposal of wastes by returning them to the soil is an ancient practice that is still popular.

1 Bunslau, Prussia irrigated with sewage in 1559.

B "Nightsoiling," the practice of returning untreated human wastes to the soil, has been important to the economy of many countries by maintaining soil productivity, but it has led to an association of unsanitary conditions with land disposal.

C Land disposal of wastes has enjoyed flourishes of popularity followed by periods of disfavor. We are now in a period of increasing interest.

III THE SOIL AS RECEPTABLE FOR WASTES

A The soil is a natural body at the earth's surface that supports or is capable of supporting plant growth. It is made up of mineral material, organic matter, biological populations, solutions, and air. It is dynamic. Volumetric composition of a typical topsoil:

Mineral matter - 45%
Air and solution - 50%
Organic matter - 5%

B A typical soil has properties which equip it to serve as an assimilator of wastes. It performs the following functions:

Filters
Buffers
Adsorbs
Transforms chemically
Transforms biologically
Supports plants that reuse nutrients contained in wastes

C Soil properties usually desirable for waste assimilation

1 Deep
2 Permeable
3 Fine textured enough to sorb ions
4 Level (except for spray runoff systems)

IV THE SLUDGE

A Digested sludge is a good fertilizer

1 Characteristics of sludge are determined by composition of wastewater, treatment processes, and the sludge conditioning and handling techniques used.

2 A suspension of organic and inorganic solids removed from wastewater.

3 Liquid sludge is high in water content. The water content varies from 90% in chemically precipitated organic sludge to 99% in activated sludge.

4 Before stabilization it contains living pathogens and putrescible organic solids.

5 Stabilization and sometimes disinfection are needed before spreading it on land.

6 It contains all essential elements for plant nutrition. Potash is low in comparison to nitrogen, and phosphate.

7 Dried sludge is not competitive with inorganic fertilizers, but a two-inch application of liquid sludge from Chicago will supply the nutrients for an average corn crop in Illinois (Dalton, 1967).

8 Fertilizer value of dried sewage sludge: (Anderson, 1955)

	Activated	Digested
Nitrogen (Average 1951-55)	5.6% of solids	2.4%
Phosphate	5.7%	

Average fertilizer value of liquid digested activated sludge from Chicago:

	% of solids by weight
Nitrogen	5
Phosphate	3
Potash	1/2

B Sludge is a good soil conditioner

1 Organic sludge matter is similar to soil humus when it is digested.

2 Sludge improves soil structure, permeability, water-holding capacity, and capacity to hold nutrients.

3 Water and other constituents of sludge may promote plant growth.

C Sludge must be stabilized before it is spread on the land.

1 Anaerobic digestion is the most popular method.

a It reduces volatile solids leaving a stable humus-like organic portion.

b Pathogens are reduced.

c Control of digesters is difficult. Poorly digested sludge is not suitable for land spreading.

2 Aerobic stabilization is a very promising method of stabilizing sludge for land spreading.

a It produces a brown, almost odorless, nitrified sludge that is very stable.

b It removes grease and reduces pathogens.

c Aerobic stabilization is popular with many small treatment plants.

d Power is required for aeration.

e Aeration is difficult with primary sludge, but easier with biological sludge.

3 Chemical stabilization

a Liming to raise pH to 11.0 for 24 hours has been effective in stabilizing sludge and killing pathogens in the laboratory. Lime sludge has promoted growth of grass in short-term greenhouse studies. Long-term results are expected to be beneficial to soils.

b Sulfur dioxide stabilized sludge in the laboratory. The sludge has not been tried on the soil but is expected to have a slight acidifying effect that can be controlled with limestone.

c Other chemicals applied to wastewater or sludge--aluminum and iron salts or organic polymers have had no detrimental effects in short-term studies. The soil clogging effect produced by the gelatinous aluminum and iron sludges is expected to be offset by the improved physical condition resulting from increased organic matter in the soil.

V WAYS OF DISPOSING OF SLUDGE BY LAND SPREADING

A Objectives include:

1 Disposal of as much sludge as possible without degrading the environment or creating a nuisance;

2 Improving low quality land;

3 Fertilize vegetation and improve soils;

4 Combinations of the first three.

The objective chosen will depend upon the kind and amount of land available, the kind and amount of sludge available, public attitude toward sludge spreading, and personal preference of officials.

B Conveyance

1 A very popular way for small treatment plants to dispose of sludge is to haul directly from the digesters to cropland or forest, and spray from a tank truck. Large volume or long hauls are expensive.

2 Barges have been used by coastal cities to transport sludge for ocean disposal. They have also been tried at Chicago. A large volume of sludge and navigable water are requirements for feasible barging. Barge transportation offers some flexibility, but sludge thickening would be needed. It also requires loading and docking facilities at the plant and docking, unloading, and distribution system at the spreading site.

3 Railroad transportation can be used if rail lines are conveniently located for the spreading site.

4 Pipelines are economical and dependable for large cities to transport sludge up to 150 miles or more. Capital costs are high but operating costs are low when compared to the other three methods.

5 Sludge is most frequently conveyed to land disposal sites by tank truck from small treatment plants and pipelines by large treatment plants.

C Application techniques

1 Irrigation methods are usually used when the objective is fertilization of vegetation.

a Ridge and furrow irrigation requires level land or grading to achieve contour furrows. It is better adapted to cold weather operation and it offers less aesthetic problems than spray irrigation.

b Spray irrigation is flexible and requires less soil preparation. It can be practiced on sloping land and with a variety of vegetative cover. The rainbird is a common type. Aerosol drift may occur.

c Flood irrigation usually requires land shaping.

d Injecting sludge into soils or plowing it in with a moldboard plow gets it out of sight and prevents odors. The methods are not adapted to continuous applications on cropland.

e Flood and till is used when crops are not on the land.

2 Disposal or reclamation of low quality land is usually done by some variety of flood and till methods.

D Loading rates -- depend upon the system -- fertilization, reclamation or disposal.

1 The proper annual application rate also depends upon sludge composition, concentration of solids, soil characteristics, climate, vegetation, and cropping practices.

a Reclamation applications up to 1000 tons per acre per year have been used successfully.

b Soil conditioner and fertilizer applications have ranged from 0.5 to 300 tons of solids per acre. Burd suggested 100 tons per acre for cropland. Lunt (1961) suggested 10 tons of solids per acre of sludge containing 2.5% nitrogen as an optimum for crops grown on medium or sandy textured soils. A general rule-of-thumb is:

Up to 100 tons per acre per year for ideal conditions
10-25 tons per acre per year for average conditions
< 5 tons per acre per year for adverse conditions

VI FACTORS DETERMINING SAFE SLUDGE DISPOSAL ON LAND

A Nature of sludge

1 Sludge containing high concentration of heavy metals or other toxic substances should not be applied to land. Some heavy metals and minor elements are toxic to plants at relatively low concentrations. Only on acid soils and with heavy applications has toxicity been experienced. Management to precipitate metals in soils may be needed.

2 High nitrogen content may lead to nitrate pollution of aquifers or surface water. Crops may remove up to 300 lbs. of nitrogen/A/-per year. Nitrogen removal may be necessary where heavy applications of sludge are made.

3 Hygienic conditions

a Digested sludge contains some living pathogens.

b Most pathogens die quickly in soil, but some may live for several weeks.

c Fruits or vegetables which grow in contact with the soil and are eaten raw should not be fertilized with sludge unless it has been disinfected.

d Disinfection may be done economically with heat, chemicals, or storage in a lagoon. Pasteurization is practiced in Europe.

e Most soils are effective filters. Water that has percolated through five feet or more of soil has been found to be free of pathogens.

B Shallow, steep, or coarse textured soils and runoff should be avoided. Wet, poorly drained soils are undesirable.

1 Erosion should be controlled to prevent sludge from washing into surface water.

C Loading rate

1 Overloading the soil can cause odors, insects, and aesthetic problems. Well stabilized sludge applied in thin applications has caused neither odor nor insect problems.

D Land use determines the precautions required.

1 Sludge applied to land that is isolated and inaccessible to the public may not require the same degree of disinfection and stabilization as sludge that is applied to recreation land or to other land accessible to the public.

2 Some cities require disinfection of sludge that is to be spread on pastures. However, spreading digested sludge on pastures has been widely practiced in this country without known outbreaks of disease.

VII ECONOMICS

A The cost of spreading sludge on land is less than for other forms of disposal for most cities and towns.

1 The net cost of drying and selling sludge as fertilizer at San Diego was $35.00 per dry ton of solids in 1951 to 1956 period. In 1959 and 1960, the cost of spreading liquid sludge on the land was $9.91 per ton (Burd, 1968).

2 Liquid sludge spreading to make productive soil out of sand at New York City was reported to cost about the same as barging to the ocean, $7.50 per ton.

3 Chicago's plan developed in 1967 compared costs of landspreading with the methods they were using and with incineration.

		Gross
Drying for fertilizer	$45.00 net	$60.00
Wet air oxidation	50.00	
Digestion and permanent lagoons	49.00	
Digestion and reclamation of farm land	15.00	
Digestion and reclamation of strip mines	16.00	

4 It is easily the most economical method for some small treatment plants. Others find drying beds with air dried sludge picked up by farmers and gardeners more economical.

VIII OBSTACLES TO SLUDGE SPREADING ON LAND

A Public resistance to accepting waste from the city on rural land forced revision of plans at Chicago, Charleston, West Virginia, and Columbus, Ohio.

1 In contrast, a number of cities charge a small fee for liquid sludge.

2 Many farmers in Pennsylvania desire more sludge than is available to them.

B Sludge spreading has no glamor or profit for the designer.

C Design criteria is lacking. Guidelines are available in the form of reports of research and successful land spreading projects, but precise design criteria is not.

D Land, whether purchased or obtained under agreement, may be difficult to get without an effective educational program.

E There is a general misconception that near many of the larger cities no open land exists that would be suitable for sludge spreading. Satisfactory land exists within about 100 miles of every city in this country.

F There are unfounded concerns about disease hazards, odors, insects, and toxic substances when sludge is applied to the soil.

G Past failures caused by unstable sludge, poor land management, and overloading of soil have tended to prejudice people against land spreading.

1 Farming should be done by farmers.

IX SOME CITIES THAT USE LAND SPREADING

A Manassas, Virginia

1 Has a 2 MGD activated sludge plant.

2 Digested sludge is trucked about three miles and spread on farm land from back of truck.

3 Pasture, hay, and some corn and small grain are grown.

4 Rate of application is about 10,000 gallons per acre per year--less than enough to meet the nutrient requirements of the crops.

5 Land spreading was adapted when alum sludge failed to dry on drying beds.

B San Diego, California

1 Mission Bay Park was created by spreading digested sludge on dredged sand from shallow bay.

2 A seven and one-half mile long 8" pipeline is used to transport sludge to Mission Bay Park.

3 Up to 1000 tons per acre of sludge has improved soil for grass and ornamental shrubs.

4 New low odor thresholds caused by luxury hotels and park use caused adoption of present drying bed technique instead of flow and till system formerly used.

5 Sludge from pipeline is spread to a depth of about 8" on 15 acres of drying beds of one and one-half acres each.

6 Supernatant from drying beds is decanted in series. Cultivation starts as soon as sludge is dry enough.

7 Dried sludge is removed from beds and stockpiled for use in parks.

8 Cost of building parkland with sludge is about 1/4 that of importing topsoil.

C Oceanside, California

1 Digested sludge is hauled by truck and dumped into a trench 3' deep and 18" wide. Although the sludge has been buried in the same area for eight years, they never see sludge in the sand. Microbial oxidation is rapid.

D Chicago, Illinois

1 The city produces about 1000 tons per day of sludge solids.

2 Sludge has been handled in four ways.

a Wet air oxidation

b Heat drying for fertilizer

c High rate digestion--lagoon storage

d Imhoff

3 Plans call for high rate digestion followed by disposal on low grade farmland.

4 Pipeline transportation was determined to be the most economical with barging second.

5 After heavy applications to build up productivity, cropland will receive 20 tons of solids per year.

6 Nitrogen has proven to be the element in sludge that will first limit sludge applications. Heavy metal accumulations have not been excessive after four years of applications.

7 Adverse public reaction has prevented full implementation of the land spreading program.

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SLUDGE COMBUSTION

I INTRODUCTION

A Incineration of municipal and industrial refuse has been a standard practice for many years. The combustion of semi-solid sewage and industrial waste sludge is a relatively recent innovation. Dearborn, Michigan, installed the first full-scale sewage sludge incinerator in 1935.(287) 2 Sludge combustion is becoming increasingly popular as land areas for sand beds, lagoons, and landfills become more difficult to find and more expensive. The land situation is magnified by ever-increasing volumes of sludge to dispose of and by the encroachment of urban neighborhoods on land disposal areas. There is no doubt that sludge combustion will in the future be adopted by more and more industries and cities because it represents a sanitary method for ultimate sludge disposal (at least for the organic portion of the sludge) in a relatively small land area. For many industries and cities, incineration will provide the only practical answer to sludge disposal.

B Incineration is practiced for two basic purposes, volume reduction and solids sterilization. Fulfilling these purposes is expensive and it may cause an air pollution problem. But the economics of combustion appear more favorable each year as the alternative sludge disposal methods become more expensive. Air pollution problems can be solved by proper equipment design and operation.

II SLUDGE CHARACTERISTICS

A Russell says the following sludge parameters are most important in the incineration process: (1) moisture, (2) volatiles, (3) inerts, and (4) calorific value.(65d) 2 Of the above, moisture is the principal characteristic over which the treatment plant operator has some control. Moisture is generally reduced by mechanical sludge-dewatering techniques before incineration. It is important because of the thermal load it imposes on the incineration process with consequent effects on self-sustained sludge combustion.

B Volatile and inert materials affect the calorie or Btu value of the sludge. They are, to some extent, controlled by other treatment processes such as degritting, mechanical dewatering, and sludge digestion. Almost all of the combustibles are present in the sludge as volatiles, much of it in the form of grease. The volatile percentage and, therefore, the heat value can vary widely, so incineration equipment must be designed to handle a broad range of values.

1 Table 19.1 by Owen describes the most important incineration parameters for many of the solids generated at a sewage treatment plant.(321)

2 As a general rule, the thermal value of sewage sludge is considered to be 10,000 Btu per pound of volatile solids. If the ultimate analysis is known, Owen claimed that the heat value can be precisely computed by using the DuLong formula:(321)

$$Q = 14,600\,C + 62,000\,(H - \frac{O}{8})$$

where Q = Btu/lb.
C = % carbon
H = % hydrogen
O = % oxygen

III THEORY

A Incineration processes involve two steps: (1) drying and (2) combustion. In addition to fuel and air; time, temperature, and turbulence are necessary for a complete reaction. The drying step should not be confused with preliminary dewatering; this dewatering, usually by mechanical means, precedes the incineration process in most systems. A sludge, having a moisture content of about 75 percent is delivered to the most common types of incinerators. Since the typical sludge contains about 3 pounds of water for each pound of dry solids, the heat required to evaporate the water nearly balances the heat available from combustion of the dry solids.(65d)

B Drying and combustion may be done in separate pieces of equipment or successively in the same unit. Manufacturers have developed widely varying types of sludge drying and combustion equipment. These include traveling-grate furnaces, rotary-kiln-type furnaces, fluidized-bed units, wet-oxidation units, atomized spray units, multiple hearth furnaces, and flash-drying units.

Table 19.1

Material	Combustibles (%)	Ash (%)	Btu/Pound
Grease and scum	88.5	11.5	16,750
Raw sewage solids	74.0	26.0	10,285
Fine screenings	86.4	13.6	8,990
Ground garbage	84.8	15.2	8,245
Digested sewage solids and ground garbage	49.6	50.4	8,020
Digested sludge	59.6	40.4	5,290
Grit	33.2	69.8	4,000

The drying and combustion process consists of the following phases: (1) raising the temperature of the feed sludge to 212°F, (2) evaporating water from the sludge, (3) increasing the water vapor and air temperature of the gas, and (4) increasing the temperature of the dried sludge volatiles to the ignition point.(65d)

C Practical operation of an incinerator requires that air in excess of theoretical requirements must be supplied for complete combustion of the fuel. The introduction of excess air has the effect of reducing the burning temperature and increasing the heat losses from the furnace. For this reason, a closely controlled minimum excess air flow is desirable for maximum thermal economy. The amount of excess air required varies with the type of burning equipment, the nature of the sludge to be burned, and the disposition of the stack gases.

D Fuel (sludge) burned in a furnace emits heat; some is absorbed by the furnace and is lost by radiation, a larger portion is lost with the stack gases, and a smaller portion is lost with the ash. The difference between the heat generated and the heat lost is available for heating the incoming sludge and air. Self-sustained combustion is often possible with dewatered raw sludges once the burning of auxiliary fuel raises incinerator temperatures to the ignition point.

E The primary end products of combustion are considered to be water, sulfur dioxide, carbon dioxide, and inert ash.

III TYPES OF FURNACE

In general, there are only three types of furnace capable of burning sewage sludge, including conditioned sludge resulting from the biological treatment of trade effluents. These are (a) the rotary drum furnace, (b) the fluidized-bed furnace, and (c) the multiple-hearth furnace.

A Rotary Drum Furnace (Figure 1)

This consists of an inclined cylinder with internal baffles which is rotated slowly by a toothed gear ring enshrouding the barrel. Sludge is admitted at the upper end and normally travels with the flow of heated combustion air. Ash and flue gases are discharged from the lower end of the drum and the exhaust gases contain about 20 per cent by weight of the ash. Because of structural difficulties in providing firebrick insulation inside the drum, the heat losses are high, which means that a well-dried cake must be produced by the preceding dewatering process in order to achieve autothermic incineration. In this state, no extraneous fuel is needed except for part-load operation or during startup.

B Fluidized-bed Furnace (Figure 2)

Fluidized-bed techniques have produced a compact form of furnace suitable for burning any material which can satisfactorily be fed to it, including sewage sludge. The bed of specially selected silica sand is maintained in a highly turbulent state by the combustion air and both the sludge and any supplementary fuel are fed directly into this zone. Combustion is completed in one or two seconds at a temperature of about 950°C.

Table 1

Effect of Moisture Level of Sludge on Auxiliary Fuel Requirement*

Per Cent Solids Wet Basis	Moisture Content Dry Basis (lb. water/lb. dry solid)	Auxiliary Heat Required (Btu/lb. dry solid)	Additional Cost ($/ton dry solid)
15	5.67	5830	5.8
20	4.0	2500	2.5
25	3.0	500	0.5
30	2.33	-833	-
35	1.85	-1780	-
40	1.5	-2500	-

*Calculation is based on sludge with heating value of 5500 Btu/lb. of dry solids. Heating requirement is estimated from water content only, using 2,000 Btu/lb. of water. Fuel is estimated to cost $0.50/million Btu.

With this type of furnace all the ash appears in the flue gases so that highly efficient gas cleaning is essential to maintain statutory requirements for gaseous discharges. Furthermore,it is necessary to incorporate a recuperative heat exchanger to pre-heat part or all of the combustible air. Since this exchanger has to handle flue gases at between 900°C and 1000°C, it is by no means cheap. It is not, therefore, economically justifiable to reduce the temperature of the exit flue gases below 700°C, which inevitably results in a poorer overall heat balance than that of the multiple-hearth incinerator.

The principal application of this type of furnace is for burning sludges with a significant content of highly volatile material such as those resulting from the treatment of oil refinery or chemical plant wastes. Its "all-up" cost is about the same as that of a multiple-hearth furnace installation for the same duty. However, it is not possible at present to build a fluidized-bed furnace with a capacity as large as that of the biggest multiple-hearth furnace, the chief obstacle being the difficulty of feeding the cake uniformly over the whole of the bed.

C Multiple-hearth Furnace (Figures 3 and 4)

This furnace consists essentially of a firebrick-lined, vertical, cylindrical shell with firebrick diaphragms or hearths set one above the other. Alternate hearths are centrally or peripherally perforated to permit the simultaneous downward flow of burning material and upward flow of burning material and upward flow of combustion gases in true counter-current fashion. A central, hollow, air-cooled rotor is fitted with air-cooled, radial, hollow rabble arms and rabble teeth and this rotates slowly about the vertical axis. This ensures that all the solids passing through the furnace are continuously raked to facilitate even combustion. Because of the counter-current flow of solids and gases, automatic pre-heating of the combustion air takes place without the need for flue gas heat exchangers. Since only about 10 per cent by weight of the ash left by combustion appears in the flue gases, much less elaborate cleaning is necessary than with the fluidized-bed furnace.

1 Furnaces of up to 7 m (roughly 23 ft.) internal diameter can be built and from four to twelve hearths are normally specified according to the duty involved. Exit gas temperatures of between 300°C and 600°C are achieved, depending on the nature of the sludge being burned.

2 Because of a phenomenon known as "thermal jump," sewage sludge being burnt in a multiple-hearth furnace exists for only a very short time in the distillation range of temperatures in which offensive-smelling vapours are generated. Although the gas phase goes through a steady temperature reduction in its upward passage through

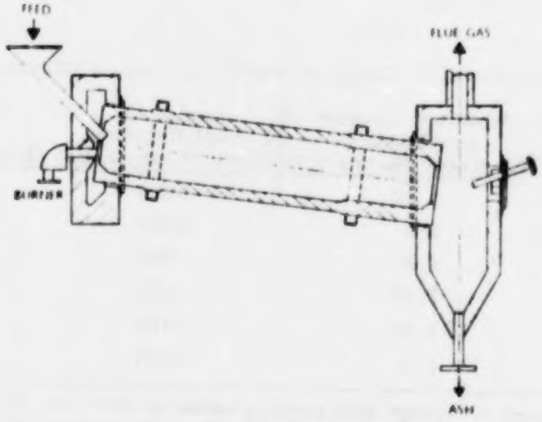
FEED
FLUE GAS
BURNER
ASH

Fig. 1. Diagram of rotary furnace

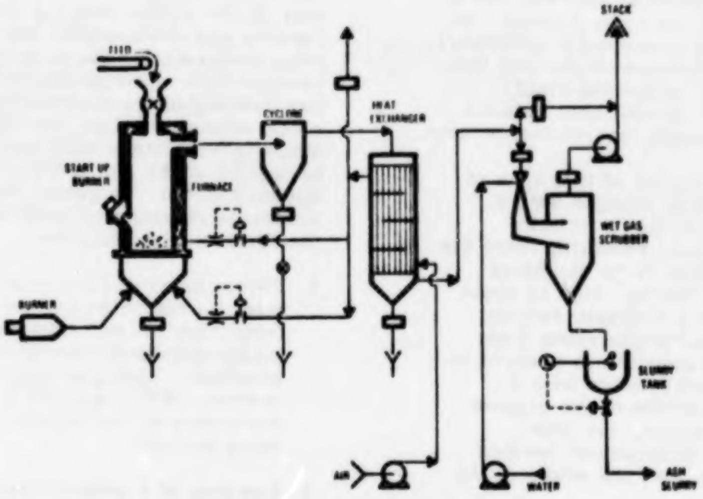
FEED
START UP BURNER
FURNACE
CYCLONE
HEAT EXCHANGER
STACK
WET GAS SCRUBBER
SLURRY TANK
BURNER
AIR
WATER
ASH SLURRY

Fig. 2. Flowsheet of fluidized bed furnace

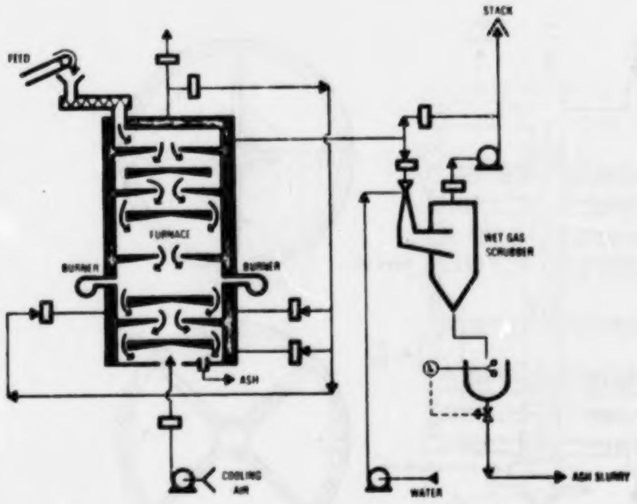

Fig. 3. Flowsheet of multiple-hearth furnace

the furnace, the descending sludge remains for most of its drying period at about 90°C because of the presence of water in the liquid phase. In the combustion zone the temperature rises rapidly to between 800°C and 900°C and essentially complete combustion takes place. The ash is normally characterized by an ignition loss at 800°C of less than 1 per cent by weight. It is odourless and sterile. Wetter sludges can be burnt more econonically in a multiple-hearth furnace than in a rotary or a fluidized-bed furnace. Autothermic incineration can be achieved with undigested primary sludge containing about 30 per cent dry solids whereas approximately 40 per cent solids would be needed in a fluidized-bed furnace.

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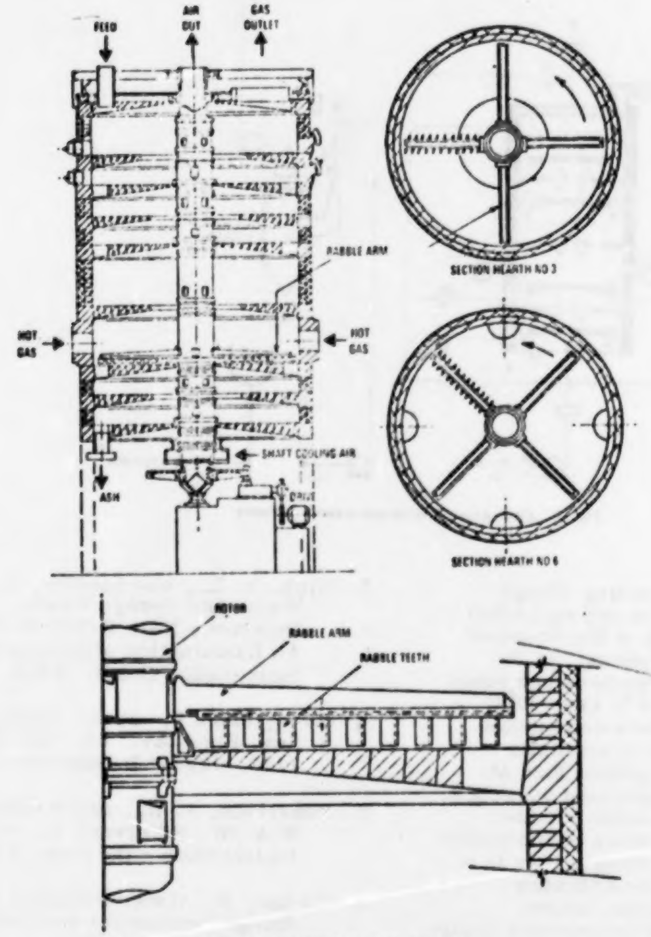
FEED
AIR OUT
GAS OUTLET
RABBLE ARM
HOT GAS
HOT GAS
SHAFT COOLING AIR
ASH
SECTION HEARTH NO 3
SECTION HEARTH NO 6
MOTOR
RABBLE ARM
RABBLE TEETH

Fig. 4. Multiple-hearth furnace